Variational *R*-matrix methods for many-electron systems: Unified relativistic theory

Radosław Szmytkowski*
Atomic Physics Division, Department of Atomic Physics and Luminescence, Faculty of Applied Physics and Mathematics, Technical University of Gdańsk, Narutowicza 11/12, PL 80-952 Gdańsk, Poland

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We use a formalism of integral operators to present a unified approach to variational *R*-matrix methods for many-electron systems described by the Dirac Hamiltonian. Variational principles for eigenvalues and matrix elements of many-electron integral operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$, which are the central objects in the approach, are listed. The Rayleigh-Ritz linear trial functions are used in these principles, yielding second-order variational estimates of eigenvalues, matrix elements, and kernels of these operators. A multiconfiguration Dirac-Hartree-Fock approach to the relativistic *R*-matrix method is proposed.

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I. INTRODUCTION

The history of the *R*-matrix method for systems described by the Dirac equation dates back to 1948 when Goertzel [1] presented a relativistic generalization of Wigner's [2] nonrelativistic formulation of the method. Since in low-energy nuclear reaction physics, for which the *R*-matrix method was originally invented, relativistic effects manifest themselves mainly through the spin-orbit coupling, which may be usually accounted for within the semirelativistic theory based on the Pauli equation, Goertzel's results were scarcely referred to. At the beginning of the 1970s, the *R*-matrix method was introduced into nonrelativistic atomic physics [3] and in 1975 Chang [4], being unaware of Goertzel's work, rederived the *R*-matrix theory for Dirac particles. Chang's numerical code implementing the Dirac *R*-matrix method was applied by its author [5,6] and, after significant development, by an Oxford-Belfast team (cf. Ref. [7] and references therein) to studies of low-energy electron collisions with heavy atomic and ionic targets and photoionization thereof. Furthermore, at the beginning of the 1990s, Thumm and Norcross [8] used their own two-electron Dirac *R*-matrix code to study low-energy electron impact on cesium atoms.

All aforementioned works utilized a particular relationship between the *R*-matrix and Green's function of an auxiliary artificial finite-volume boundary value problem involving a many-electron Dirac equation. In 1991, Hamacher and Hinze [9] proposed an entirely different approach to the relativistic *R*-matrix theory of atomic systems, based on a variational principle for reciprocals of eigenvalues of the relativistic *R*-matrix. Their proposal is a direct extension to the relativistic case of the nonrelativistic eigenchannel *R*-matrix method, which during the past two decades has evolved into one of the most powerful methods of analyzing Rydberg spectra and photoionization of atoms and small molecules (cf. Refs. [10–12] and references therein). The *R*-matrix eigenchannel approach itself falls into a wider class of variational *R*-matrix methods (cf. Refs. [13–17] and references therein).

Some time ago, a collaboration aimed at developing a new atomic code based on the relativistic variational *R*-matrix approach was established with the present author's participation. Starting the project, we did not foresee any particular problems, save for some eventual numerical ones, since the mathematical background of the relativistic *R*-matrix theory seemed to be sound. However, already at the very preliminary stage, making acquaintance with the existing literature of the subject, we found an error in the Goertzel-Chang formulation of the Dirac *R*-matrix theory. Since it was not obvious at that moment whether the difficulty encountered did afflict the variational approaches or not, we attempted to clarify the situation seeking an origin of the problem with a hope to remove it. We succeeded but found that the corrected Goertzel-Chang theory [16,18–20] appeared to be mathematically much more complicated than that presented in Refs. [1, 4], being most efficiently formulated in the language of integral operators rather than matrices. Although the variational approaches appeared to be free of the distressing difficulty, the mathematical effort undertaken had also far-reaching consequences for our project: we realized that the operator language is ideally suited for providing a unified treatment of variational *R*-matrix methods for many-electron relativistic systems [21]. Such a unified treatment is presented in the current paper, in which we consider a system that may be either a complete electronic cloud of a many-electron relativistic atom, a molecule, an ion, or a group of valence electrons, the interactions of which with a nucleus (or nuclei) and with an electronic core have been modeled somehow. Since it has been our intention to keep the presentation as general as possible, in this work we do not refer to any possible symmetries that might simplify considerations at the cost of their generality.

The work is divided into ten sections. After this Introduction, in Sec. II we acquaint the reader with the mathematical notation to be used later. In Sec. III we set up the physical problem and in Sec. IV we introduce two linear integral operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and study their properties. Then in Sec. V we define and investigate the operators $\hat{\mathcal{R}}^{(\pm)}(E)$ that are the generalized inverses of $\hat{\mathcal{B}}^{(\pm)}(E)$. Section VI is devoted to showing that, if a suitable functional basis set is used, the only nonzero submatrix of the matrix representing $\hat{\mathcal{R}}^{(+)}(E)$ in that basis coincides with the relativistic *R*-matrix appear-

*Electronic address: radek@mif.pg.gda.pl

ing in earlier matrix approaches to the theory [9,18,19]. In Sec. VII we list six variational principles for eigenvalues and matrix elements of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$. Details of derivations of these principles are omitted since they are completely analogous to those for the single-particle theory presented in Refs. [15, 16]. Variational principles are known to be convenient tools for approximate calculations, and in Sec. VIII we describe how the Rayleigh-Ritz linear trial functions may be employed in the principles listed in Sec. VII to obtain convenient estimates of eigenvalues, matrix elements, and integral kernels of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$. In Sec. IX we show that, after suitable modifications, the variational principles for eigenvalues of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$ may be used to derive two sets of multiconfiguration Dirac-Hartree-Fock *R*-matrix equations, solutions to which yield optimal approximate wave functions describing a system under consideration within the *R*-matrix hypervolume as well as variational estimates of eigenvalues of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$. The work ends with a brief summary in Sec. X.

II. DEFINITIONS AND NOTATION

Let $\mathcal{V}\subset\mathbb{R}^3$ be a finite volume enclosed by a surface $\mathcal{S}$. A position vector, relative to some reference origin, of a point in the volume $\mathcal{V}$ will be denoted by $\mathbf{r}$. If the point is located on the surface $\mathcal{S}$, the position vector will be marked with $\boldsymbol{\rho}$.

If $\phi(\mathbf{r})$ and $\phi'(\mathbf{r})$ are any two sufficiently regular four-component spinor functions, their scalar products over $\mathcal{V}$ and $\mathcal{S}$ are defined as

$$\langle\phi|\phi'\rangle\equiv\int_{\mathcal{V}}d^3\mathbf{r}\,\phi^{\dagger}(\mathbf{r})\phi'(\mathbf{r}) \tag{2.1}$$

and

$$(\phi|\phi')\equiv\oint_{\mathcal{S}}d^2\boldsymbol{\rho}\,\phi^{\dagger}(\boldsymbol{\rho})\phi'(\boldsymbol{\rho}), \tag{2.2}$$

respectively. Here $d^3\mathbf{r}$ is an infinitesimal volume element of $\mathcal{V}$ around the point $\mathbf{r}$, $d^2\boldsymbol{\rho}$ is an infinitesimal *scalar* surface element of $\mathcal{S}$ around the point $\boldsymbol{\rho}$, while the dagger denotes the matrix Hermitian conjugation.

With the volume $\mathcal{V}\subset\mathbb{R}^3$, one may associate a hypervolume $\mathfrak{V}\subset\mathbb{R}^{3N}$ defined as

$$\mathfrak{V}=\{\mathfrak{r}=[\mathbf{r}_1,\ldots,\mathbf{r}_K,\ldots,\mathbf{r}_N]\in\mathbb{R}^{3N};\ \ \forall\ \ 1\leqslant K\leqslant N:\mathbf{r}_K\in\mathcal{V}\} \tag{2.3}$$

or, equivalently, as the N-fold Cartesian product of $\mathcal{V}$,

$$\mathfrak{V}=\mathcal{V}^N\equiv\mathcal{V}_1\times\cdots\times\mathcal{V}_N. \tag{2.4}$$

The hypervolume $\mathfrak{V}$ is bounded by a hypersurface $\mathfrak{S}$,

$$\mathfrak{S}=\bigcup_{K=1}^{N}\mathcal{V}_1\times\cdots\times\mathcal{V}_{K-1}\times\mathcal{S}_K\times\mathcal{V}_{K+1}\times\cdots\times\mathcal{V}_N. \tag{2.5}$$

If the point $\mathfrak{r}$ lies on the hypersurface $\mathfrak{S}$, we shall denote this using the symbol ϱ instead of $\mathfrak{r}$. A unit outward vector normal to the hypersurface $\mathfrak{S}$ at the point ϱ will be denoted by $\mathbf{n}(\varrho)$.

The hypersurface $\mathfrak{S}$ is composed of N geometrically similar hyperfacets, with the Kth hyperfacet $\mathfrak{S}_K$ defined as

$$\mathfrak{S}_K=\mathcal{V}_1\times\cdots\times\mathcal{V}_{K-1}\times\mathcal{S}_K\times\mathcal{V}_{K+1}\times\cdots\times\mathcal{V}_N\qquad(K=1,2,...,N). \tag{2.6}$$

If the point ϱ is on $\mathfrak{S}_K$, we shall indicate this adding the subscript K at ϱ, i.e., writing ϱ_K instead of ϱ. Explicitly,

$$\varrho_K=[\mathbf{r}_1,\ldots,\mathbf{r}_{K-1},\boldsymbol{\rho}_K,\mathbf{r}_{K+1},\ldots,\mathbf{r}_N]. \tag{2.7}$$

It follows from the definition of $\mathfrak{S}_K$ and from Eq. (2.7) that on $\mathfrak{S}_K$ the unit outward normal vector is

$$\mathbf{n}(\varrho_K)=[\mathbf{0}_1,\ldots,\mathbf{0}_{K-1},\mathbf{n}(\boldsymbol{\rho}_K),\mathbf{0}_{K+1},\ldots,\mathbf{0}_N], \tag{2.8}$$

where $\mathbf{n}(\boldsymbol{\rho})$ is a unit outward vector normal to $\mathcal{S}$ at the point $\boldsymbol{\rho}$.

If $\Phi(\mathfrak{r})$ and $\Phi'(\mathfrak{r})$ are sufficiently regular 4^N-component spinor functions defined in $\mathfrak{V}$ and on $\mathfrak{S}$, their scalar products over $\mathfrak{V}$ and over $\mathfrak{S}$ are

$$\langle\Phi|\Phi'\rangle_{\mathfrak{V}}\equiv\int_{\mathfrak{V}}d^{3N}\mathfrak{r}\,\Phi^{\dagger}(\mathfrak{r})\Phi'(\mathfrak{r}), \tag{2.9}$$

$$(\Phi|\Phi')_{\mathfrak{S}}\equiv\oint_{\mathfrak{S}}d^{3N-1}\varrho\,\Phi^{\dagger}(\varrho)\Phi'(\varrho), \tag{2.10}$$

respectively, where

$$\int_{\mathfrak{V}}d^{3N}\mathfrak{r}\ \ (\cdots)\equiv\int_{\mathcal{V}}d^3\mathbf{r}_1\cdots\int_{\mathcal{V}}d^3\mathbf{r}_N\ \ (\cdots) \tag{2.11}$$

and

$$\oint_{\mathfrak{S}}d^{3N-1}\varrho\ \ (\cdots)\equiv\sum_{K=1}^{N}\int_{\mathfrak{S}_K}d^{3N-1}\varrho_K\ \ (\cdots) \tag{2.12}$$

with

$$\int_{\mathfrak{S}_K}d^{3N-1}\varrho_K\ \ (\cdots)\equiv\int_{\mathcal{V}}d^3\mathbf{r}_1\cdots\int_{\mathcal{V}}d^3\mathbf{r}_{K-1}\oint_{\mathcal{S}}d^2\boldsymbol{\rho}_K\times\int_{\mathcal{V}}d^3\mathbf{r}_{K+1}\cdots\int_{\mathcal{V}}d^3\mathbf{r}_N\ \ (\cdots). \tag{2.13}$$

Here $d^{3N}\mathfrak{r}$ denotes an infinitesimal element of the hypervolume $\mathfrak{V}$ around the point $\mathfrak{r}$ and $d^{3N-1}\varrho$ is an infinitesimal *scalar* element of the hypersurface $\mathfrak{S}$ around the point ϱ. The scalar product of the functions $\Phi(\varrho)$ and $\Phi'(\varrho)$ over a particular hyperfacet $\mathfrak{S}_K$ is defined as

$$(\Phi|\Phi')_{\mathfrak{S}_K}\equiv\int_{\mathfrak{S}_K}d^{3N-1}\varrho_K\ \ \Phi^{\dagger}(\varrho_K)\Phi'(\varrho_K). \tag{2.14}$$

From Eqs. (2.10), (2.12), and (2.14) one has

$$(\Phi|\Phi')_{\mathfrak{S}}=\sum_{K=1}^{N}(\Phi|\Phi')_{\mathfrak{S}_K}. \tag{2.15}$$

A space of all completely antisymmetric 4^N-component spinor functions $\Phi(\mathfrak{r})$ defined in the hypervolume $\mathfrak{V}$ and such that $\langle\Phi|\Phi\rangle_{\mathfrak{V}}<\infty$ will be denoted by $\mathcal{A}_{\mathfrak{V}}$. The projector on the space of such functions (the hypervolume antisymmetrizer) will be marked with $\hat{\mathcal{A}}_{\mathfrak{V}}$. A class of functions from $\mathcal{A}_{\mathfrak{V}}$ that are at least once differentiable in $\mathfrak{V}$ will be designed with $\mathcal{A}'_{\mathfrak{V}}$. A space of all completely antisymmetric functions $\Phi(\varrho)$ defined on the hypersurface $\mathfrak{S}$ and such that $(\Phi|\Phi)_{\mathfrak{S}}<\infty$ will be denoted by $\mathcal{A}_{\mathfrak{S}}$; the projector on the space of such functions (the hypersurface antisymmetrizer) will be marked with $\hat{\mathcal{A}}_{\mathfrak{S}}$.

If $\Phi(\varrho)$ and $\Phi'(\varrho)$ are any two functions from $\mathcal{A}_{\mathfrak{S}}$, from their antisymmetry and from the geometric similarity of any two hyperfacets $\mathfrak{S}_K$ and $\mathfrak{S}_{K'}$ one infers that

$$(\Phi|\Phi')_{\mathfrak{S}_K}=(\Phi|\Phi')_{\mathfrak{S}_{K'}} \quad \forall \quad 1\leqslant K,K'\leqslant N$$

$$[\Phi(\varrho),\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}] \tag{2.16}$$

and consequently [cf. Eq. (2.15)]

$$(\Phi|\Phi')_{\mathfrak{S}_K}=\frac{1}{N}(\Phi|\Phi')_{\mathfrak{S}} \quad \forall \quad 1\leqslant K\leqslant N$$

$$[\Phi(\varrho),\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}]. \tag{2.17}$$

III. THE MANY-ELECTRON DIRAC HAMILTONIAN AND THE HYPERSURFACE OPERATORS $\hat{\mathcal{E}}_{\perp}^{(\pm)}$ AND $\hat{\mathcal{B}}^{(\pm)}$

Consider an N-electron system described by the Dirac Hamiltonian

$$\begin{aligned}\hat{\mathcal{H}}(\mathfrak{r})&=\sum_{K=1}^{N}\hat{H}(\mathbf{r}_K)+\tfrac{1}{2}\sum_{\substack{K,K'=1\\(K\neq K')}}^{N}U(\mathbf{r}_K,\mathbf{r}_{K'})\\&=\sum_{K=1}^{N}[-ic\hbar\boldsymbol{\mathcal{E}}_K\cdot\boldsymbol{\nabla}_K+\mathcal{B}_K mc^2+V(\mathbf{r}_K)]\\&\quad+\tfrac{1}{2}\sum_{\substack{K,K'=1\\(K\neq K')}}^{N}U(\mathbf{r}_K,\mathbf{r}_{K'}).\end{aligned} \tag{3.1}$$

In this definition, $\mathbf{r}_K$ is a position vector of the Kth electron in physical space, $\boldsymbol{\nabla}_K$ is the gradient operator with respect to spatial coordinates of the Kth electron, and $\mathfrak{r}=[\mathbf{r}_1,\ldots,\mathbf{r}_N]$ is a position hypervector of a point describing a configuration of the system in an abstract $3N$-dimensional configuration space. The one- and two-electron potential functions $V(\mathbf{r}_K)$ and $U(\mathbf{r}_K,\mathbf{r}_{K'})$ are real scalar spin-independent functions of electronic spatial coordinates with $U(\mathbf{r}_K,\mathbf{r}_{K'})$ assumed to be symmetric in its arguments. The $4^N\times4^N$ matrices $\boldsymbol{\mathcal{E}}_K$ and $\mathcal{B}_K$ are defined in terms of the 4×4 matrices

$$\mathcal{I}=\begin{pmatrix}I&O\\O&I\end{pmatrix},\quad \boldsymbol{\alpha}=\begin{pmatrix}O&\boldsymbol{\sigma}\\\boldsymbol{\sigma}&O\end{pmatrix},\quad \beta=\begin{pmatrix}I&O\\O&-I\end{pmatrix} \tag{3.2}$$

[here I and O are the 2×2 unit and null matrices, respectively, and $\boldsymbol{\sigma}=[\sigma_x,\sigma_y,\sigma_z]$ is a vector composed of the 2×2 Pauli matrices] in the following way:

$$\boldsymbol{\mathcal{E}}_K=\mathcal{I}_1\otimes\cdots\otimes\mathcal{I}_{K-1}\otimes\boldsymbol{\alpha}_K\otimes\mathcal{I}_{K+1}\otimes\cdots\otimes\mathcal{I}_N, \tag{3.3}$$

$$\mathcal{B}_K=\mathcal{I}_1\otimes\cdots\otimes\mathcal{I}_{K-1}\otimes\beta_K\otimes\mathcal{I}_{K+1}\otimes\cdots\otimes\mathcal{I}_N, \tag{3.4}$$

where $\otimes$ denotes the direct (Kronecker's) matrix product. Subscripts at the matrices on the right-hand sides of Eqs. (3.3) and (3.4) refer to particular electrons.

Throughout the rest of this work, we shall be concerned with the time-independent Dirac equation

$$[\hat{\mathcal{H}}(\mathfrak{r})-E]\Psi(E,\mathfrak{r})=0, \tag{3.5}$$

in which E is a *preselected* total energy of the system, including rest energies of the electrons, and the wave function $\Psi(E,\mathfrak{r})$ is a 4^N-component column vector. Since we are dealing with electrons, we shall conform to Pauli's exclusion principle and consider only those solutions to Eq. (3.5) that are completely antisymmetric 4^N-component spinors. In what follows, we shall assume that the electronic energy E is fixed at some prescribed real value and consider those configurations of the system when all N electrons are in some fictitious finite volume $\mathcal{V}$ enclosed by a surface $\mathcal{S}$. Then the configuration point $\mathfrak{r}$ lies in the corresponding (fictitious) hypervolume $\mathfrak{V}$ defined by Eq. (2.3) and bounded by the hypersurface $\mathfrak{S}$ defined by Eq. (2.5). We emphasize that we do *not* confine the electrons to the volume $\mathcal{V}$ in any way since we do not impose any artificial boundary condition on the wave function $\Psi(E,\mathfrak{r})$ at the hypersurface $\mathfrak{S}$.

We shall denote by $\mathcal{A}_{\mathfrak{V}}(E)$ a subspace of $\mathcal{A}_{\mathfrak{V}}$ built of all completely antisymmetric solutions to the Dirac equation (3.5) in the hypervolume $\mathfrak{V}$ at the real energy E; the projector on this subspace will be denoted by $\hat{\mathcal{A}}_{\mathfrak{V}}(E)$. For later convenience, we define also a subspace $\mathcal{A}_{\mathfrak{S}}(E)\subset\mathcal{A}_{\mathfrak{S}}$,

$$\mathcal{A}_{\mathfrak{S}}(E)=\{\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}};\exists\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E):\ \Phi(\varrho)=\Psi(E,\varrho)\}. \tag{3.6}$$

Let $\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$ and $\Psi'(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$. Then, by virtue of reality of E, we have

$$\langle\hat{\mathcal{H}}\Psi'|\Psi\rangle_{\mathfrak{V}}=\langle\Psi'|\hat{\mathcal{H}}\Psi\rangle_{\mathfrak{V}}, \tag{3.7}$$

which implies that the Hamiltonian $\hat{\mathcal{H}}$ is Hermitian on $\mathcal{A}_{\mathfrak{V}}(E)$. On the other hand, by virtue of the explicit form of the Hamiltonian, after applying the $3N$-dimensional Gauss integration theorem, we obtain

$$\langle\hat{\mathcal{H}}\Psi'|\Psi\rangle_{\mathfrak{V}}-\langle\Psi'|\hat{\mathcal{H}}\Psi\rangle_{\mathfrak{V}}=(\Psi'|ic\hbar\hat{\mathcal{E}}_{\perp}\Psi)_{\mathfrak{S}}, \tag{3.8}$$

where $\hat{\mathcal{E}}_{\perp}$ is a linear integral operator, defined on $\mathcal{A}_{\mathfrak{S}}$, with the kernel

$$\text{Æ}_\perp(\varrho,\varrho')=\text{æ}_\perp(\varrho)\delta^{(3N-1)}(\varrho-\varrho'), \tag{3.9}$$

where

$$\text{æ}_\perp(\varrho)=\mathbf{n}(\varrho)\cdot\text{Æ},\quad \text{Æ}=[\text{æ}_1,\ldots,\text{æ}_N]. \tag{3.10}$$

It is clear that $\hat{\text{Æ}}_\perp$ is local and Hermitian under the hypersurface scalar product $(|)_{\mathfrak{S}}$. Equations (3.7) and (3.8) yield

$$(\Psi'|i\hat{\text{Æ}}_\perp\Psi)_{\mathfrak{S}}=0. \tag{3.11}$$

To proceed further, we introduce two linear operators $\hat{ß}^{(+)}$ and $\hat{ß}^{(-)}$ such that for any sufficiently regular (not necessarily antisymmetric) 4^N-component function $\Phi(\varrho)$ defined on $\mathfrak{S}$, one has

$$\hat{ß}^{(\pm)}\Phi(\varrho_K)=ß_K^{(\pm)}\Phi(\varrho_K), \tag{3.12}$$

where

$$ß_K^{(\pm)}=\mathcal{I}_1\otimes\cdots\otimes\mathcal{I}_{K-1}\otimes\beta_K^{(\pm)}\otimes\mathcal{I}_{K+1}\otimes\cdots\otimes\mathcal{I}_N \tag{3.13}$$

with

$$\beta^{(\pm)}=\tfrac{1}{2}(\mathcal{I}\pm\beta). \tag{3.14}$$

It is clear that $\hat{ß}^{(\pm)}$ are Hermitian under the scalar product $(|)_{\mathfrak{S}}$ and that

$$\hat{ß}^{(+)}+\hat{ß}^{(-)}=\hat{1},\quad \hat{ß}^{(\pm)}\hat{ß}^{(\pm)}=\hat{ß}^{(\pm)},\quad \hat{ß}^{(\pm)}\hat{ß}^{(\mp)}=0 \tag{3.15}$$

(here $\hat{1}$ denotes the unit operator), which implies that $\hat{ß}^{(\pm)}$ are orthogonal projectors. Then, we define two linear integral operators

$$\hat{\text{Æ}}_\perp^{(\pm)}=\hat{ß}^{(\pm)}\hat{\text{Æ}}_\perp. \tag{3.16}$$

Obviously, if $\Phi(\varrho)$ is any sufficiently regular (again, not necessarily antisymmetric) 4^N-component function defined on the hypersurface $\mathfrak{S}$, we have

$$\hat{\text{Æ}}_\perp^{(\pm)}\Phi(\varrho_K)=\text{æ}_{\perp K}^{(\pm)}(\varrho_K)\Phi(\varrho_K), \tag{3.17}$$

where

$$\text{æ}_{\perp K}^{(\pm)}(\varrho_K)=ß_K^{(\pm)}\text{æ}_\perp(\varrho_K)=\mathcal{I}_1\otimes\cdots\otimes\mathcal{I}_{K-1}\otimes\alpha_{\perp K}^{(\pm)}(\boldsymbol{\rho}_K)\otimes\mathcal{I}_{K+1}\otimes\cdots\otimes\mathcal{I}_N \tag{3.18}$$

with

$$\alpha_\perp^{(\pm)}(\boldsymbol{\rho})=\mathbf{n}(\boldsymbol{\rho})\cdot\beta^{(\pm)}\boldsymbol{\alpha}. \tag{3.19}$$

It follows from Eqs. (3.15)–(3.19) and from the well-known properties of the Dirac matrices $\boldsymbol{\alpha}$ and β [22] that

$$\hat{\text{Æ}}_\perp^{(+)}+\hat{\text{Æ}}_\perp^{(-)}=\hat{\text{Æ}}_\perp,\quad \hat{\text{Æ}}_\perp^{(\pm)\ddagger}=\hat{\text{Æ}}_\perp^{(\mp)} \tag{3.20}$$

[here ‡ denotes the operator Hermitian conjugation with respect to the scalar product $(|)_{\mathfrak{S}}$],

$$\hat{\text{Æ}}_\perp^{(\pm)}\hat{\text{Æ}}_\perp^{(\pm)}=0,\quad \hat{\text{Æ}}_\perp^{(\pm)}\hat{\text{Æ}}_\perp^{(\mp)}=\hat{ß}^{(\pm)}, \tag{3.21}$$

$$\hat{\text{Æ}}_\perp^{(\pm)}\hat{ß}^{(\pm)}=0,\quad \hat{ß}^{(\pm)}\hat{\text{Æ}}_\perp^{(\pm)}=\hat{\text{Æ}}_\perp^{(\pm)}, \tag{3.22}$$

$$\hat{ß}^{(\pm)}\hat{\text{Æ}}_\perp^{(\mp)}=0,\quad \hat{\text{Æ}}_\perp^{(\pm)}\hat{ß}^{(\mp)}=\hat{\text{Æ}}_\perp^{(\pm)}. \tag{3.23}$$

The advantage of introducing the operators $\hat{\text{Æ}}_\perp^{(\pm)}$ is that with their aid, by virtue of the relations (3.20), Eq. (3.11) may be rewritten in two equivalent forms,

$$(i\hat{\text{Æ}}_\perp^{(\pm)}\Psi'|\Psi)_{\mathfrak{S}}=(\Psi'|i\hat{\text{Æ}}_\perp^{(\pm)}\Psi)_{\mathfrak{S}}. \tag{3.24}$$

Equation (3.24) means that the operators $i\hat{\text{Æ}}_\perp^{(\pm)}$ are Hermitian *on the domain* $\mathcal{A}_{\mathfrak{S}}(E)$.

IV. OPERATORS $\hat{\mathcal{B}}^{(\pm)}(E)$

The key role in the rest of this paper, and in the whole *R*-matrix theory for many-electron systems described by the Dirac Hamiltonian (3.1), is played by two linear integral operators $\hat{\mathcal{B}}^{(+)}(E)$ and $\hat{\mathcal{B}}^{(-)}(E)$, defined on $\mathcal{A}_{\mathfrak{S}}$, such that if $\Psi(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$, then

$$i\hat{\text{Æ}}_\perp^{(\pm)}\Psi(E,\varrho)=\gamma^{(\pm)}\hat{\mathcal{B}}^{(\pm)}(E)\Psi(E,\varrho). \tag{4.1}$$

The coefficients

$$\gamma^{(\pm)}=\pm\left(\frac{\hbar}{2mc}\right)^{\pm1}, \tag{4.2}$$

related by $\gamma^{(+)}\gamma^{(-)}=-1$, have been set off in Eq. (4.1) for later convenience. The operators $\hat{\mathcal{B}}^{(\pm)}(E)$ are represented by their integral kernels $\mathcal{B}^{(\pm)}(E,\varrho,\varrho')$, in terms of which Eq. (4.1) may be rewritten equivalently as

$$i\hat{\text{Æ}}_\perp^{(\pm)}\Psi(E,\varrho)=\gamma^{(\pm)}\oint_{\mathfrak{S}}d^{3N-1}\varrho'\,\mathcal{B}^{(\pm)}(E,\varrho,\varrho')\Psi(E,\varrho'). \tag{4.3}$$

Making use of Eq. (4.1) in the relations (3.24), one has

$$(\hat{\mathcal{B}}^{(\pm)}\Psi'|\Psi)_{\mathfrak{S}}=(\Psi'|\hat{\mathcal{B}}^{(\pm)}\Psi)_{\mathfrak{S}}, \tag{4.4}$$

which means that the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ are Hermitian with respect to the scalar product $(|)_{\mathfrak{S}}$. One easily shows also that

$$\hat{ß}^{(\pm)}\hat{\mathcal{B}}^{(\pm)}(E)\hat{ß}^{(\pm)}=\hat{\mathcal{B}}^{(\pm)}(E) \tag{4.5}$$

and that

$$\hat{\mathcal{B}}^{(\pm)}(E)=\hat{\mathcal{A}}_{\mathfrak{S}}\hat{\mathcal{B}}^{(\pm)}(E)\hat{\mathcal{A}}_{\mathfrak{S}}, \tag{4.6}$$

which means that the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ are symmetric in all the *N* electrons.

Consider next a subset $\{\Psi_n(E,\mathfrak{r})\}\subset\mathcal{A}_{\mathfrak{V}}(E)$ such that for any function from this set on the hypersurface $\mathfrak{S}$, it holds that

$$i\hat{\text{Æ}}_\perp^{(+)}\Psi_n(E,\varrho)=\gamma^{(+)}b_n(E)\hat{ß}^{(+)}\Psi_n(E,\varrho), \tag{4.7}$$

where $\{b_n(E)\}$ are numbers that, in general, are different for different functions from the set $\{\Psi_n(E,\mathfrak{r})\}$. Operating on Eq. (4.7) from the left with the operator $i\hat{\mathcal{E}}_\perp^{(-)}$ and utilizing the second of Eqs. (3.21) and the second of Eqs. (3.23), after simple manipulations we obtain

$$i\hat{\mathcal{E}}_\perp^{(-)}\Psi_n(E,\varrho)=\gamma^{(-)}b_n^{-1}(E)\hat{\beta}^{(-)}\Psi_n(E,\varrho). \quad (4.8)$$

Next, utilizing Eq. (4.1) defining the operators $\hat{\mathcal{B}}^{(\pm)}(E)$, the relations (4.7) and (4.8) may be rewritten as

$$\hat{\mathcal{B}}^{(\pm)}(E)\Psi_n(E,\varrho)=b_n^{\pm 1}(E)\hat{\beta}^{(\pm)}\Psi_n(E,\varrho), \quad (4.9)$$

which implies that the hypersurface functions $\{\Psi_n(E,\varrho)\}$ may be considered as simultaneous eigenfunctions of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$, with the singular non-negative operator weights $\hat{\beta}^{(\pm)}$, and the constants $\{b_n^{\pm 1}(E)\}$ may be considered as corresponding eigenvalues. Since the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\beta}^{(\pm)}$ are Hermitian under the hypersurface scalar product $(|)_{\mathfrak{S}}$, in the standard way one shows that the eigenvalues $\{b_n^{\pm 1}(E)\}$ are real while eigenfunctions associated with different eigenvalues obey the following orthogonality relations over the hypersurface $\mathfrak{S}$:

$$(\Psi_n|\hat{\beta}^{(\pm)}\Psi_{n'})_{\mathfrak{S}}=0 \quad [b_n(E)\neq b_{n'}(E)]. \quad (4.10)$$

Since for any two eigenfunctions one has

$$(\Psi_n|\hat{\beta}^{(-)}\Psi_{n'})_{\mathfrak{S}}=(\gamma^{(+)})^2 b_n(E)b_{n'}(E)(\Psi_n|\hat{\beta}^{(+)}\Psi_{n'})_{\mathfrak{S}}, \quad (4.11)$$

in the rest of the paper, without any loss of generality, we shall assume that eigenfunctions associated with degenerate eigenvalues (if there are any) are also orthogonal under the scalar product $(|)_{\mathfrak{S}}$ so that

$$(\Psi_n|\hat{\beta}^{(\pm)}\Psi_{n'})_{\mathfrak{S}}=0 \quad (n\neq n'). \quad (4.12)$$

The spectral expansions of the kernels $\mathcal{B}^{(\pm)}(E,\varrho,\varrho')$ in terms of the eigenfunctions $\{\Psi_n(E,\varrho)\}$ and the eigenvalues $\{b_n^{\pm 1}(E)\}$ are

$$\mathcal{B}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_n \frac{\beta_K^{(\pm)}\Psi_n(E,\varrho_K)b_n^{\pm 1}(E)\Psi_n^\dagger(E,\varrho'_{K'})\beta_{K'}^{(\pm)}}{(\Psi_n|\hat{\beta}^{(\pm)}\Psi_n)_{\mathfrak{S}}} \quad (4.13)$$

or equivalently, due to Eq. (3.17),

$$\mathcal{B}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_n \frac{\alpha_{\perp K}^{(\pm)}(\varrho_K)\Psi_n(E,\varrho_K)b_n^{\pm 1}(E)\Psi_n^\dagger(E,\varrho'_{K'})\alpha_{\perp K'}^{(\mp)}(\varrho'_{K'})}{(\Psi_n|\hat{\beta}^{(\mp)}\Psi_n)_{\mathfrak{S}}}. \quad (4.14)$$

The sets $\{\hat{\beta}^{(\pm)}\Psi_n(E,\varrho)\}$ are complete in the subspaces $\mathcal{A}_{\mathfrak{S}}^{(\pm)}(E)\subset\mathcal{A}_{\mathfrak{S}}$ defined as

$$\mathcal{A}_{\mathfrak{S}}^{(\pm)}(E)=\{\hat{\beta}^{(\pm)}\Psi(E,\varrho):\Psi(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)\}. \quad (4.15)$$

Since for any $\Psi(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ we have

$$\Psi(E,\varrho)=\hat{\beta}^{(+)}\Psi(E,\varrho)+\hat{\beta}^{(-)}\Psi(E,\varrho) \quad (4.16)$$

[cf. the first of Eqs. (3.15)], the set $\{\hat{\beta}^{(+)}\Psi_n(E,\varrho)\}\cup\{\hat{\beta}^{(-)}\Psi_n(E,\varrho)\}$ is complete in $\mathcal{A}_{\mathfrak{S}}(E)$ and the following expansion holds:

$$\Psi(E,\varrho)=\sum_n c_n^{(+)}(E)\hat{\beta}^{(+)}\Psi_n(E,\varrho)+\sum_n c_n^{(-)}(E)\hat{\beta}^{(-)}\Psi_n(E,\varrho) \quad (4.17)$$

with the expansion coefficients, due to Eq. (4.12), given by

$$c_n^{(\pm)}(E)=\frac{(\Psi_n|\hat{\beta}^{(\pm)}\Psi)_{\mathfrak{S}}}{(\Psi_n|\hat{\beta}^{(\pm)}\Psi_n)_{\mathfrak{S}}}. \quad (4.18)$$

At first sight it seems that the coefficients $c_n^{(+)}(E)$ and $c_n^{(-)}(E)$ are different. We notice, however, that since $\Psi(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$, on utilizing the second of Eqs. (3.21), the second of Eqs. (3.20), and Eq. (4.7), we have

$$(\Psi_n|\hat{\beta}^{(-)}\Psi)_{\mathfrak{S}}=\gamma^{(+)}b_n(E)(\Psi_n|i\hat{\mathcal{E}}_\perp^{(+)}\Psi)_{\mathfrak{S}}. \quad (4.19)$$

Since $\Psi_n(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Psi(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$, we know from Eq. (3.24) that in Eq. (4.19) the action of the operator $i\hat{\mathcal{E}}_\perp^{(+)}$ may be transferred to the left. Then, applying the eigenequation (4.7), substituting the result into Eq. (4.18), and making use of Eq. (4.11), we find

$$c_n^{(-)}(E)=c_n^{(+)}(E). \quad (4.20)$$

Consequently, the expansion (4.17) may be rewritten in either of the two forms

$$\Psi(E,\varrho)=\sum_n \frac{(\Psi_n|\hat{\beta}^{(\pm)}\Psi)_{\mathfrak{S}}}{(\Psi_n|\hat{\beta}^{(\pm)}\Psi_n)_{\mathfrak{S}}}\Psi_n(E,\varrho). \quad (4.21)$$

The expansion analogous to Eq. (4.21) holds also in the hypervolume $\mathfrak{V}$: for any $\Psi(E,\mathfrak{r})\in\mathcal{A}_{\mathfrak{V}}(E)$, one has

$$\Psi(E,\mathfrak{r})=\sum_n \frac{(\Psi_n|\hat{\beta}^{(\pm)}\Psi)_{\mathfrak{S}}}{(\Psi_n|\hat{\beta}^{(\pm)}\Psi_n)_{\mathfrak{S}}}\Psi_n(E,\mathfrak{r}). \quad (4.22)$$

We conclude this section observing that from the eigenfunctions $\{\Psi_n(E,\varrho)\}$ and the eigenvalues $\{b_n(E)\}$ one may construct kernels of the operators $\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E)$ projecting on the subspaces $\mathcal{A}^{(\pm)}_{\mathfrak{S}}(E)$:

$$\mathcal{A}^{(\pm)}_{\mathfrak{S}}(E,\varrho_K,\varrho'_{K'})=\sum_n \frac{ß^{(\pm)}_K\Psi_n(E,\varrho_K)\Psi^{\dagger}_n(E,\varrho'_{K'})ß^{(\pm)}_{K'}}{(\Psi_n|\hat{ß}^{(\pm)}\Psi_n)_{\mathfrak{S}}}. \tag{4.23}$$

Notice that for any $\Psi(E,\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ one has

$$\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E)\Psi(E,\varrho)=\hat{ß}^{(\pm)}\Psi(E,\varrho) \tag{4.24}$$

and that

$$\hat{\mathcal{B}}^{(\pm)}(E)=\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E)\hat{\mathcal{B}}^{(\pm)}(E)\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E). \tag{4.25}$$

V. OPERATORS $\hat{\mathcal{R}}^{(\pm)}(E)$

The relation (4.5) implies that the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ do not have inverses in the ordinary sense. However, we may define their generalized inverses $\hat{\mathcal{R}}^{(\pm)}(E)$, possessing the properties

$$\hat{\mathcal{R}}^{(\pm)}(E)=\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E)\hat{\mathcal{R}}^{(\pm)}(E)\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E), \tag{5.1}$$

through the reciprocity relations

$$\hat{\mathcal{R}}^{(\pm)}(E)\hat{\mathcal{B}}^{(\pm)}(E)=\hat{\mathcal{B}}^{(\pm)}(E)\hat{\mathcal{R}}^{(\pm)}(E)=\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E). \tag{5.2}$$

The operators $\hat{\mathcal{R}}^{(\pm)}(E)$ are represented by their integral kernels $\mathcal{R}^{(\pm)}(E,\varrho,\varrho')$, in terms of which the definition (5.2) reads

$$\begin{aligned}\oint_{\mathfrak{S}} d^{3N-1}\varrho''\ \ \mathcal{R}^{(\pm)}(E,\varrho,\varrho'')\mathcal{B}^{(\pm)}(E,\varrho'',\varrho') &= \oint_{\mathfrak{S}} d^{3N-1}\varrho''\ \ \mathcal{B}^{(\pm)}(E,\varrho,\varrho'')\mathcal{R}^{(\pm)}(E,\varrho'',\varrho') \\ &= \mathcal{A}^{(\pm)}_{\mathfrak{S}}(E,\varrho,\varrho').\end{aligned} \tag{5.3}$$

Since $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E)$ are Hermitian with respect to the scalar product $(|)_{\mathfrak{S}}$, $\hat{\mathcal{R}}^{(\pm)}(E)$ are also Hermitian. Moreover, $\hat{\mathcal{R}}^{(\pm)}(E)$ possess properties analogous to those characterizing $\hat{\mathcal{B}}^{(\pm)}(E)$ and expressed in Eqs. (4.5) and (4.6).

With the aid of the operators $\hat{\mathcal{R}}^{(\pm)}(E)$, on utilizing Eq. (4.24), Eq. (4.1) may be rewritten in the form

$$\hat{ß}^{(\pm)}\Psi(E,\varrho)=-\gamma^{(\mp)}\hat{\mathcal{R}}^{(\pm)}(E)i\hat{Æ}^{(\pm)}_{\perp}\Psi(E,\varrho). \tag{5.4}$$

Eigenequations for $\hat{\mathcal{R}}^{(\pm)}(E)$ are obtained after acting with these operators from the left on Eq. (4.9) and making use of Eq. (4.24). One finds

$$\hat{\mathcal{R}}^{(\pm)}(E)\Psi_n(E,\varrho)=b_n^{\mp 1}(E)\hat{ß}^{(\pm)}\Psi_n(E,\varrho). \tag{5.5}$$

Equation (5.5) and the orthogonality relations (4.12) imply the spectral expansions

$$\mathcal{R}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_n \frac{ß^{(\pm)}_K\Psi_n(E,\varrho_K)b_n^{\mp 1}(E)\Psi^{\dagger}_n(E,\varrho'_{K'})ß^{(\pm)}_{K'}}{(\Psi_n|\hat{ß}^{(\pm)}\Psi_n)_{\mathfrak{S}}}. \tag{5.6}$$

From Eqs. (4.14) and (5.6), one infers the following relationships between the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\mp)}(E)$:

$$\hat{\mathcal{B}}^{(\pm)}(E)=\hat{Æ}^{(\pm)}_{\perp}\hat{\mathcal{R}}^{(\mp)}(E)\hat{Æ}^{(\mp)}_{\perp}. \tag{5.7}$$

VI. MATRIX REPRESENTATIONS OF THE OPERATORS $\hat{\mathcal{B}}^{(\pm)}(E)$ AND $\hat{\mathcal{R}}^{(\pm)}(E)$

Assume now that a functional set $\{\Phi_i(\varrho)\}$, forming an orthonormal basis in $\mathcal{A}_{\mathfrak{S}}(E)$, is given. In this basis the kernels $\mathcal{B}^{(\pm)}(E,\varrho,\varrho')$ and $\mathcal{R}^{(\pm)}(E,\varrho,\varrho')$ have the bilinear expansions

$$\mathcal{B}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_{i,j} ß^{(\pm)}_K\Phi_i(\varrho_K)(\Phi_i|\hat{\mathcal{B}}^{(\pm)}\Phi_j)_{\mathfrak{S}} \times\Phi^{\dagger}_j(\varrho'_{K'})ß^{(\pm)}_{K'}, \tag{6.1}$$

$$\mathcal{R}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_{i,j} ß^{(\pm)}_K\Phi_i(\varrho_K)(\Phi_i|\hat{\mathcal{R}}^{(\pm)}\Phi_j)_{\mathfrak{S}} \times\Phi^{\dagger}_j(\varrho'_{K'})ß^{(\pm)}_{K'} \tag{6.2}$$

with the expansion coefficients $\{(\Phi_i|\hat{\mathcal{B}}^{(\pm)}\Phi_j)_{\mathfrak{S}}\}$ and $\{(\Phi_i|\hat{\mathcal{R}}^{(\pm)}\Phi_j)_{\mathfrak{S}}\}$ forming square matrices $\mathsf{B}^{(\pm)}(E)$ and $\mathsf{R}^{(\pm)}(E)$, respectively. These matrices are mutually reciprocal in the sense of

$$\mathsf{R}^{(\pm)}(E)\mathsf{B}^{(\pm)}(E)=\mathsf{B}^{(\pm)}(E)\mathsf{R}^{(\pm)}(E)=\mathsf{A}^{(\pm)}(E) \tag{6.3}$$

[cf. the operator relation (5.2)] and are additionally related by

$$\mathsf{B}^{(\pm)}(E)=\text{Æ}^{(\pm)}_{\perp}\mathsf{R}^{(\mp)}(E)\text{Æ}^{(\mp)}_{\perp} \tag{6.4}$$

[cf. Eq. (5.7)], where $\mathsf{A}^{(\pm)}(E)$ and $\text{Æ}^{(\pm)}_{\perp}$ are square matrices with elements $\{(\Phi_i|\hat{\mathcal{A}}^{(\pm)}_{\mathfrak{S}}(E)\Phi_j)_{\mathfrak{S}}\}$ and $\{(\Phi_i|\hat{Æ}^{(\pm)}_{\perp}\Phi_j)_{\mathfrak{S}}\}$, respectively.

Projecting operator equations (4.1) and (5.4) from the left on the basis functions $\{\Phi_i(\varrho)\}$ yields their matrix representations

$$\mathsf{Q}^{(\pm)}(E)=\gamma^{(\pm)}\mathsf{B}^{(\pm)}(E)\mathsf{P}^{(\pm)}(E), \tag{6.5}$$

$$\mathsf{P}^{(\pm)}(E)=-\gamma^{(\mp)}\mathsf{R}^{(\pm)}(E)\mathsf{Q}^{(\pm)}(E), \tag{6.6}$$

where $\mathsf{P}^{(\pm)}(E)$ and $\mathsf{Q}^{(\pm)}(E)$ are column matrices with elements $\{(\Phi_i|\hat{ß}^{(\pm)}\Psi)_{\mathfrak{S}}\}$ and $\{(\Phi_i|i\hat{Æ}^{(\pm)}_{\perp}\Psi)_{\mathfrak{S}}\}$, respectively, related through

$$\mathsf{Q}^{(\pm)}(E)=i\text{Æ}^{(\pm)}_{\perp}\mathsf{P}^{(\mp)}(E). \tag{6.7}$$

The matrices $\mathsf{B}^{(\pm)}(E)$ and $\mathsf{R}^{(\pm)}(E)$ are highly singular and therefore inconvenient for use in potential applications. To overcome this singularity problem, it is convenient to choose the following particular form of the basis $\{\Phi_i(\varrho)\}$:

$$\{\Phi_i(\varrho)\}=\{\Phi_{i'}^{(+)}(\varrho)\}\cup\{\Phi_{i''}^{(-)}(\varrho)\}, \tag{6.8}$$

where the functions in the subsets $\{\Phi_i^{(\pm)}(\varrho)\}$ are such that

$$\hat{\mathcal{A}}_{\mathfrak{S}}^{(\pm)}(E)\Phi_i^{(\pm)}(\varrho)=\Phi_i^{(\pm)}(\varrho), \quad \hat{\mathcal{A}}_{\mathfrak{S}}^{(\pm)}(E)\Phi_i^{(\mp)}(\varrho)=0. \tag{6.9}$$

Obviously,

$$(\Phi_i^{(\pm)}|\Phi_j^{(\pm)})_{\mathfrak{S}}=\delta_{ij}, \quad (\Phi_i^{(\pm)}|\Phi_j^{(\mp)})_{\mathfrak{S}}=0. \tag{6.10}$$

In what follows, we shall assume that the basis functions have been arranged in such an order that a matrix of any relevant operator $\hat{\mathsf{Op}}$ in this basis has the form

$$\mathsf{Op}=\begin{pmatrix}\mathsf{Op}^{(++)} & \mathsf{Op}^{(+-)}\\ \mathsf{Op}^{(-+)} & \mathsf{Op}^{(--)}\end{pmatrix}, \tag{6.11}$$

where $\mathsf{Op}^{(++)}$ is a square submatrix with elements $\{(\Phi_i^{(+)}|\hat{\mathsf{Op}}\Phi_j^{(+)})_{\mathfrak{S}}\}$; the other submatrices of Op are defined analogously. In the particular basis (6.8), the matrices $\mathsf{B}^{(\pm)}(E)$, $\mathsf{R}^{(\pm)}(E)$, $\mathsf{A}^{(\pm)}(E)$, and $\text{Æ}_\perp^{(\pm)}$ are

$$\mathsf{B}^{(+)}(E)=\begin{pmatrix}\mathsf{B}^{(+)}(E) & 0\\ 0 & 0\end{pmatrix}, \quad \mathsf{B}^{(-)}(E)=\begin{pmatrix}0 & 0\\ 0 & \mathsf{B}^{(-)}(E)\end{pmatrix}, \tag{6.12}$$

$$\mathsf{R}^{(+)}(E)=\begin{pmatrix}\mathsf{R}^{(+)}(E) & 0\\ 0 & 0\end{pmatrix}, \quad \mathsf{R}^{(-)}(E)=\begin{pmatrix}0 & 0\\ 0 & \mathsf{R}^{(-)}(E)\end{pmatrix}, \tag{6.13}$$

$$\mathsf{A}^{(+)}(E)=\begin{pmatrix}\mathsf{I} & 0\\ 0 & 0\end{pmatrix}, \quad \mathsf{A}^{(-)}(E)=\begin{pmatrix}0 & 0\\ 0 & \mathsf{I}\end{pmatrix}, \tag{6.14}$$

$$\text{Æ}_\perp^{(+)}=\begin{pmatrix}0 & \text{Æ}_\perp^{(+)}\\ 0 & 0\end{pmatrix}, \quad \text{Æ}_\perp^{(-)}=\begin{pmatrix}0 & 0\\ \text{Æ}_\perp^{(-)} & 0\end{pmatrix}. \tag{6.15}$$

Here I and 0 are the unit and the null square submatrices, respectively. In terms of the submatrices $\mathsf{B}^{(\pm)}(E)$, $\mathsf{R}^{(\pm)}(E)$, and $\text{Æ}_\perp^{(\pm)}$, the relations (6.3) and (6.4) may be rewritten as

$$\mathsf{R}^{(\pm)}(E)\mathsf{B}^{(\pm)}(E)=\mathsf{B}^{(\pm)}(E)\mathsf{R}^{(\pm)}(E)=\mathsf{I}, \tag{6.16}$$

$$\mathsf{B}^{(\pm)}(E)=\text{Æ}_\perp^{(\pm)}\mathsf{R}^{(\mp)}(E)\text{Æ}_\perp^{(\mp)}. \tag{6.17}$$

Moreover, in the basis (6.8) the matrices $\mathsf{P}^{(\pm)}(E)$ and $\mathsf{Q}^{(\pm)}(E)$ are

$$\mathsf{P}^{(+)}(E)=\begin{pmatrix}\mathsf{P}^{(+)}(E)\\ 0\end{pmatrix}, \quad \mathsf{P}^{(-)}(E)=\begin{pmatrix}0\\ \mathsf{P}^{(-)}(E)\end{pmatrix}, \tag{6.18}$$

$$\mathsf{Q}^{(+)}(E)=\begin{pmatrix}\mathsf{Q}^{(+)}(E)\\ 0\end{pmatrix}, \quad \mathsf{Q}^{(-)}(E)=\begin{pmatrix}0\\ \mathsf{Q}^{(-)}(E)\end{pmatrix}, \tag{6.19}$$

respectively, with 0 denoting here the column null submatrix and with the submatrices $\mathsf{P}^{(\pm)}(E)$ and $\mathsf{Q}^{(\mp)}(E)$ related through

$$\mathsf{Q}^{(\pm)}(E)=i\text{Æ}_\perp^{(\pm)}\mathsf{P}^{(\mp)}(E). \tag{6.20}$$

This implies the following simplified forms of the matrix relations (6.5) and (6.6):

$$\mathsf{Q}^{(\pm)}(E)=\gamma^{(\pm)}\mathsf{B}^{(\pm)}(E)\mathsf{P}^{(\pm)}(E), \tag{6.21}$$

$$\mathsf{P}^{(\pm)}(E)=-\gamma^{(\mp)}\mathsf{R}^{(\pm)}(E)\mathsf{Q}^{(\pm)}(E). \tag{6.22}$$

Further simplifications follow if one chooses the basis (6.8) so that

$$i\text{Æ}_\perp^{(+)}=\mathsf{I}, \quad i\text{Æ}_\perp^{(-)}=-\mathsf{I}. \tag{6.23}$$

In this case, Eq. (6.17) becomes

$$\mathsf{B}^{(\pm)}(E)=\mathsf{R}^{(\mp)}(E), \tag{6.24}$$

the reciprocity relation (6.16) reads

$$\mathsf{R}^{(\pm)}(E)\mathsf{R}^{(\mp)}(E)=\mathsf{B}^{(\pm)}(E)\mathsf{B}^{(\mp)}(E)=\mathsf{I}, \tag{6.25}$$

while the relation (6.20) transforms to

$$\mathsf{Q}^{(\pm)}(E)=\pm\mathsf{P}^{(\mp)}(E). \tag{6.26}$$

At this moment, it is convenient to denote

$$\mathsf{B}(E)=\mathsf{B}^{(+)}(E)=[\mathsf{B}^{(-)}(E)]^{-1}, \tag{6.27}$$

$$\mathsf{R}(E)\equiv\mathsf{R}^{(+)}(E)=[\mathsf{R}^{(-)}(E)]^{-1}, \tag{6.28}$$

$$\mathsf{P}(E)\equiv\mathsf{P}^{(+)}(E)=-\mathsf{Q}^{(-)}(E), \tag{6.29}$$

$$\mathsf{Q}(E)\equiv\mathsf{Q}^{(+)}(E)=\mathsf{P}^{(-)}(E). \tag{6.30}$$

Then

$$\mathsf{B}(E)=\mathsf{R}^{-1}(E) \tag{6.31}$$

and

$$\mathsf{P}(E)=-\gamma^{(-)}\mathsf{R}(E)\mathsf{Q}(E). \tag{6.32}$$

Equation (6.32) establishes a relationship between the operator approach to the many-electron relativistic *R*-matrix theory elaborated in this work and earlier matrix formulations of the method [9,18,19].

VII. VARIATIONAL PRINCIPLES FOR EIGENVALUES AND MATRIX ELEMENTS OF THE OPERATORS $\hat{\mathcal{B}}^{(\pm)}(E)$ AND $\hat{\mathcal{R}}^{(\pm)}(E)$

In this section we present variational principles for eigenvalues and matrix elements of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and

$\hat{\mathcal{R}}^{(\pm)}(E)$. The principles are presented without details of their derivations, which are completely analogous to those for the single-particle problem considered in Refs. [15, 16].

A. Variational principles for eigenvalues of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ [and $\hat{\mathcal{R}}^{(\mp)}(E)$]

The variational principles for eigenvalues of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ [and $\hat{\mathcal{R}}^{(\mp)}(E)$] are

$$b^{\pm 1}(E)=\operatorname*{stat}_{\overline{\Psi}}\left\{-\gamma^{(\mp)}\frac{(\overline{\Psi}|i\hat{\mathcal{A}}_{\perp}^{(\pm)}\overline{\Psi})_{\mathfrak{S}}}{(\overline{\Psi}|\hat{\mathcal{B}}^{(\pm)}\overline{\Psi})_{\mathfrak{S}}}-\frac{\gamma^{(\mp)}}{c\hbar}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\overline{\Psi}|\hat{\mathcal{B}}^{(\pm)}\overline{\Psi})_{\mathfrak{S}}}\right\}. \tag{7.1}$$

The trial function $\overline{\Psi}(\mathfrak{r})$ is to be varied in $\mathcal{A}'_{\mathfrak{V}}$ without any other restrictions imposed on it. Stationary points of the functionals in Eq. (7.1) are eigenvalues of $\hat{\mathcal{B}}^{(\pm)}(E)$ [and $\hat{\mathcal{R}}^{(\mp)}(E)$], and trial functions yielding these values are those solutions to the Dirac equation (3.5) that on the hypersurface $\mathfrak{S}$ are corresponding (simultaneous) eigenfunctions of these operators in the sense of Eq. (4.9) [and Eq. (5.5)]. If the trial function $\overline{\Psi}(\mathfrak{r})$ is varied freely, the principle provides *all* eigenvalues and eigenfunctions of $\hat{\mathcal{B}}^{(\pm)}(E)$ [and $\hat{\mathcal{R}}^{(\mp)}(E)$] and this explains why we have not added any subscript at $b^{\pm 1}(E)$ on the left of Eq. (7.1). It is easily verifiable that the principles (7.1) have the advantage in yielding *real* estimates of eigenvalues $\{b_n^{\pm 1}(E)\}$ for *any* particular trial function used. That variational principle that corresponds to the choice of the upper superscripts in Eq. (7.1) was proposed about a decade ago by Hamacher and Hinze [9].

B. Variational principles for matrix elements of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$

Let $\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ [unlike in Sec. VI, from now on these functions need not be orthogonal with respect to the scalar product $(|)_{\mathfrak{S}}$]. The variational principles for the matrix elements $(\Phi|\hat{\mathcal{B}}^{(\pm)}\Phi')_{\mathfrak{S}}$ are

$$\begin{aligned}(\Phi|\hat{\mathcal{B}}^{(\pm)}\Phi')_{\mathfrak{S}}=\operatorname*{stat}_{\overline{\Psi}^{(\pm)},\overline{\Psi}'^{(\pm)}}\Big\{&-\gamma^{(\mp)}(\Phi|i\hat{\mathcal{A}}_{\perp}^{(\pm)}\overline{\Psi}'^{(\pm)})_{\mathfrak{S}}\\&-\gamma^{(\mp)}(i\hat{\mathcal{A}}_{\perp}^{(\pm)}\overline{\Psi}^{(\pm)}|\Phi')_{\mathfrak{S}}\\&+\gamma^{(\mp)}(i\hat{\mathcal{A}}_{\perp}^{(\pm)}\overline{\Psi}^{(\pm)}|\overline{\Psi}^{(\pm)})_{\mathfrak{S}}\\&-\frac{\gamma^{(\mp)}}{c\hbar}\langle\overline{\Psi}^{(\pm)}|[\hat{\mathcal{H}}-E]\overline{\Psi}'^{(\pm)}\rangle_{\mathfrak{V}}\Big\}.\end{aligned} \tag{7.2}$$

The trial functions $\overline{\Psi}^{(\pm)}(\mathfrak{r})$ and $\overline{\Psi}'^{(\pm)}(\mathfrak{r})$ may be varied freely in $\mathcal{A}'_{\mathfrak{V}}$. The functionals on the right of Eq. (7.2) are stationary for $\overline{\Psi}^{(\pm)}(\mathfrak{r})=\Psi^{(\pm)}(E,\mathfrak{r})$ and $\overline{\Psi}'^{(\pm)}(\mathfrak{r})=\Psi'^{(\pm)}(E,\mathfrak{r})$, where $\Psi^{(\pm)}(E,\mathfrak{r})$ and $\Psi'^{(\pm)}(E,\mathfrak{r})$ are those particular completely antisymmetric solutions to the Dirac equation (3.5) that on the hypersurface $\mathfrak{S}$ obey the boundary conditions

$$\begin{aligned}\hat{\mathcal{B}}^{(\pm)}\Psi^{(\pm)}(E,\varrho)&=\hat{\mathcal{B}}^{(\pm)}\Phi(\varrho),\\ \hat{\mathcal{B}}^{(\pm)}\Psi'^{(\pm)}(E,\varrho)&=\hat{\mathcal{B}}^{(\pm)}\Phi'(\varrho),\end{aligned} \tag{7.3}$$

respectively. It is to be emphasized that the trial functions $\overline{\Psi}^{(\pm)}(\mathfrak{r})$ and $\overline{\Psi}'^{(\pm)}(\mathfrak{r})$ need *not* satisfy boundary relations analogous to those in Eq. (7.3).

C. Variational principles for matrix elements of the operators $\hat{\mathcal{R}}^{(\pm)}(E)$

Let $\Phi(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$ and $\Phi'(\varrho)\in\mathcal{A}_{\mathfrak{S}}(E)$. The variational principles for the matrix elements $(\Phi|\hat{\mathcal{R}}^{(\pm)}\Phi')_{\mathfrak{S}}$ are

$$\begin{aligned}(\Phi|\hat{\mathcal{R}}^{(\pm)}\Phi')_{\mathfrak{S}}=\operatorname*{stat}_{\overline{\Psi}^{(\pm)},\overline{\Psi}'^{(\pm)}}\Big\{&(\Phi|\hat{\mathcal{B}}^{(\pm)}\overline{\Psi}'^{(\pm)})_{\mathfrak{S}}\\&+(\hat{\mathcal{B}}^{(\pm)}\overline{\Psi}^{(\pm)}|\Phi')_{\mathfrak{S}}\\&+\gamma^{(\mp)}(\overline{\Psi}^{(\pm)}|i\hat{\mathcal{A}}_{\perp}^{(\pm)}\overline{\Psi}'^{(\pm)})_{\mathfrak{S}}\\&+\frac{\gamma^{(\mp)}}{c\hbar}\langle\overline{\Psi}^{(\pm)}|[\hat{\mathcal{H}}-E]\overline{\Psi}'^{(\pm)}\rangle_{\mathfrak{V}}\Big\}.\end{aligned} \tag{7.4}$$

The trial functions $\overline{\Psi}^{(\pm)}(\mathfrak{r})$ and $\overline{\Psi}'^{(\pm)}(\mathfrak{r})$ may be any functions from $\mathcal{A}'_{\mathfrak{V}}$. The stationary values of the functionals in Eq. (7.4) are obtained for $\overline{\Psi}^{(\pm)}(\mathfrak{r})=\Psi^{(\pm)}(E,\mathfrak{r})$ and $\overline{\Psi}'^{(\pm)}(\mathfrak{r})=\Psi'^{(\pm)}(E,\mathfrak{r})$, with $\Psi^{(\pm)}(E,\mathfrak{r})$ and $\Psi'^{(\pm)}(E,\mathfrak{r})$ denoting those particular completely antisymmetric solutions to the Dirac equation (3.5) that on the hypersurface $\mathfrak{S}$ satisfy the boundary conditions

$$\begin{aligned}i\hat{\mathcal{A}}_{\perp}^{(\pm)}\Psi^{(\pm)}(E,\varrho)&=\gamma^{(\pm)}\hat{\mathcal{B}}^{(\pm)}\Phi(\varrho),\\ i\hat{\mathcal{A}}_{\perp}^{(\pm)}\Psi'^{(\pm)}(E,\varrho)&=\gamma^{(\pm)}\hat{\mathcal{B}}^{(\pm)}\Phi'(\varrho),\end{aligned} \tag{7.5}$$

respectively. The trial functions $\overline{\Psi}^{(\pm)}(\mathfrak{r})$ and $\overline{\Psi}'^{(\pm)}(\mathfrak{r})$ need *not* satisfy conditions analogous to those in Eq. (7.5).

VIII. DERIVATION OF VARIATIONAL ESTIMATES OF EIGENVALUES, MATRIX ELEMENTS, AND KERNELS OF THE OPERATORS $\hat{\mathcal{R}}^{(\pm)}(E)$ AND $\hat{\mathcal{B}}^{(\pm)}(E)$ WITH THE USE OF LINEAR TRIAL FUNCTIONS

A. Estimates of eigenvalues of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\mp)}(E)$

Let us use the linear trial function

$$\overline{\Psi}(\mathfrak{r})=\sum_{i=1}^{m}\overline{a}_i\Theta_i(\mathfrak{r}) \tag{8.1}$$

in the functionals

$$F^{(\pm)}[\bar{\Psi}]=-\gamma^{(\mp)}\frac{(\bar{\Psi}|i\hat{\mathcal{E}}_{\perp}^{(\pm)}\bar{\Psi})_{\mathfrak{S}}}{(\bar{\Psi}|\hat{\mathcal{B}}^{(\pm)}\bar{\Psi})_{\mathfrak{S}}}-\frac{\gamma^{(\mp)}}{c\hbar}\frac{\langle\bar{\Psi}|[\hat{\mathcal{H}}-E]\bar{\Psi}\rangle_{\mathfrak{V}}}{(\bar{\Psi}|\hat{\mathcal{B}}^{(\pm)}\bar{\Psi})_{\mathfrak{S}}} \tag{8.2}$$

[cf. the right side of Eq. (7.1)]. Substitution of Eq. (8.1) into Eq. (8.2) yields

$$F^{(\pm)}[\bar{\mathsf{a}}^{\dagger},\bar{\mathsf{a}}]=\frac{\bar{\mathsf{a}}^{\dagger}\mathsf{S}^{(\pm)}\bar{\mathsf{a}}}{\bar{\mathsf{a}}^{\dagger}\mathsf{M}^{(\pm)}\bar{\mathsf{a}}}, \tag{8.3}$$

where $\bar{\mathsf{a}}$ is an m-component column matrix with elements $\{\bar{a}_i\}$, $\bar{\mathsf{a}}^{\dagger}$ is its Hermitian conjugate, $\mathsf{S}^{(\pm)}(E)$ are $m\times m$ Hermitian matrices with elements

$$S_{ij}^{(\pm)}(E)=-\gamma^{(\mp)}(\Theta_i|i\hat{\mathcal{E}}^{(\pm)}\Theta_j)_{\mathfrak{S}}-\frac{\gamma^{(\mp)}}{c\hbar}\langle\Theta_i|[\hat{\mathcal{H}}-E]\Theta_j\rangle_{\mathfrak{V}}, \tag{8.4}$$

while $\mathsf{M}^{(\pm)}$ are $m\times m$ Hermitian matrices with elements

$$M_{ij}^{(\pm)}=(\Theta_i|\hat{\mathcal{B}}^{(\pm)}\Theta_j)_{\mathfrak{S}}. \tag{8.5}$$

We shall denote by $\tilde{\mathsf{a}}^{(\pm)\dagger}$ and $\tilde{\mathsf{a}}^{(\pm)}$ those vectors $\bar{\mathsf{a}}^{(\pm)\dagger}$ and $\bar{\mathsf{a}}^{(\pm)}$ for which the stationarity of the functionals (8.3) is attained, i.e.,

$$\delta F^{(\pm)}[\tilde{\mathsf{a}}^{(\pm)\dagger},\tilde{\mathsf{a}}^{(\pm)}]=0, \tag{8.6}$$

and by $\widetilde{b^{\pm 1}}$ the corresponding stationary values

$$\widetilde{b^{\pm 1}}=\frac{\tilde{\mathsf{a}}^{(\pm)\dagger}\mathsf{S}^{(\pm)}\tilde{\mathsf{a}}^{(\pm)}}{\tilde{\mathsf{a}}^{(\pm)\dagger}\mathsf{M}^{(\pm)}\tilde{\mathsf{a}}^{(\pm)}}, \tag{8.7}$$

which are the second-order variational estimates of eigenvalues of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\mp)}(E)$. From Eq. (8.3) we find that the conditions for $F^{(\pm)}[\bar{\mathsf{a}}^{(\pm)\dagger},\bar{\mathsf{a}}^{(\pm)}]$ to be stationary at $\tilde{\mathsf{a}}^{(\pm)\dagger}$ and $\tilde{\mathsf{a}}^{(\pm)}$ are

$$\mathsf{S}^{(\pm)}\tilde{\mathsf{a}}^{(\pm)}=\widetilde{b^{\pm 1}}\mathsf{M}^{(\pm)}\tilde{\mathsf{a}}^{(\pm)},\quad \tilde{\mathsf{a}}^{(\pm)\dagger}\mathsf{S}^{(\pm)}=\widetilde{b^{\pm 1}}\tilde{\mathsf{a}}^{(\pm)\dagger}\mathsf{M}^{(\pm)}. \tag{8.8}$$

We see that the numbers $\widetilde{b^{\pm 1}}$ are eigenvalues while the vectors $\tilde{\mathsf{a}}^{(\pm)\dagger}$ and $\tilde{\mathsf{a}}^{(\pm)}$ are, respectively, associated left and right eigenvectors of the generalized algebraic eigenvalue problems (8.8). Since the matrices $\mathsf{S}^{(\pm)}$ are functions of energy E, eigensolutions to the problems (8.8) are also energy-dependent and we shall mark this occasionally.

The number of eigenvalues $\tilde{b}(E)$ is equal to rank $\mathsf{M}^{(+)}$ and the number of eigenvalues $\widetilde{b^{-1}}(E)$ is equal to rank $\mathsf{M}^{(-)}$ [23]; in general, for a given finite basis set $\{\Theta_i(\mathfrak{r})\}$ one has rank $\mathsf{M}^{(+)}\neq$ rank $\mathsf{M}^{(-)}$. If $\tilde{b}_n(E)$ is a variational approximate of the particular eigenvalue $b_n(E)$ of $\hat{\mathcal{B}}^{(+)}(E)$ and $\hat{\mathcal{R}}^{(-)}(E)$, and if $\widetilde{b_n^{-1}}(E)$ is a variational approximate of the corresponding eigenvalue $b_n^{-1}(E)$ of $\hat{\mathcal{B}}^{(-)}(E)$ and $\hat{\mathcal{R}}^{(+)}(E)$, in general one has $\tilde{b}_n^{-1}(E)\neq\widetilde{b_n^{-1}}(E)$.

The hermiticity of $\mathsf{S}^{(\pm)}(E)$ and $\mathsf{M}^{(\pm)}$ guarantees that the eigenvalues $\{\widetilde{b_n^{\pm 1}}(E)\}$ are real and that the following orthogonality relations hold:

$$\tilde{\mathsf{a}}_n^{(\pm)\dagger}(E)\mathsf{M}^{(\pm)}\tilde{\mathsf{a}}_{n'}^{(\pm)}(E)=0\quad[\widetilde{b_n^{\pm 1}}(E)\neq\widetilde{b_{n'}^{\pm 1}}(E)]. \tag{8.9}$$

We shall assume that eigenvectors associated with degenerate eigenvalues (if there are any) have also been orthogonalized so that

$$\tilde{\mathsf{a}}_n^{(\pm)\dagger}(E)\mathsf{M}^{(\pm)}\tilde{\mathsf{a}}_{n'}^{(\pm)}(E)=0\quad(n\neq n'). \tag{8.10}$$

Then it is easy to show that the approximate eigenfunctions

$$\tilde{\Psi}_n^{(\pm)}(E,\mathfrak{r})=\sum_{i=1}^{m}\tilde{a}_{in}^{(\pm)}(E)\Theta_i(\mathfrak{r})\quad(n=1,2,\ldots,\text{rank }\mathsf{M}^{(\pm)}) \tag{8.11}$$

obey the orthogonality relations

$$(\tilde{\Psi}_n^{(\pm)}|\hat{\mathcal{B}}^{(\pm)}\tilde{\Psi}_{n'}^{(\pm)})_{\mathfrak{S}}=0\quad(n\neq n'). \tag{8.12}$$

B. Estimates of matrix elements and kernels of $\hat{\mathcal{R}}^{(\pm)}(E)$

The approximate eigenfunctions $\{\tilde{\Psi}_n^{(+)}(E,\mathfrak{r})\}$ and $\{\tilde{\Psi}_n^{(-)}(E,\mathfrak{r})\}$ found in Sec. VIII A appear to be particularly well suited for use as basis functions for variational determination of approximations to matrix elements of the operators $\hat{\mathcal{R}}^{(+)}(E)$ and $\hat{\mathcal{R}}^{(-)}(E)$, respectively. Indeed, if the trial functions of the form

$$\bar{\Psi}'^{(\pm)}(\mathfrak{r})=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\pm)}}\bar{c}_n^{(\pm)}\tilde{\Psi}_n^{(\pm)}(E,\mathfrak{r}),$$
$$\bar{\Psi}'^{(\pm)}(\mathfrak{r})=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\pm)}}\bar{c}_n'^{(\pm)}\tilde{\Psi}_n^{(\pm)}(E,\mathfrak{r}) \tag{8.13}$$

are used in the functionals

$$\begin{aligned}F^{(\pm)}[\Phi,\Phi';\bar{\Psi}^{(\pm)},\bar{\Psi}'^{(\pm)}]=&(\Phi|\hat{\mathcal{B}}^{(\pm)}\bar{\Psi}'^{(\pm)})_{\mathfrak{S}}\\&+(\hat{\mathcal{B}}^{(\pm)}\bar{\Psi}^{(\pm)}|\Phi')_{\mathfrak{S}}\\&+\gamma^{(\mp)}(\bar{\Psi}^{(\pm)}|i\hat{\mathcal{E}}_{\perp}^{(\pm)}\bar{\Psi}'^{(\pm)})_{\mathfrak{S}}\\&+\frac{\gamma^{(\mp)}}{c\hbar}\langle\bar{\Psi}^{(\pm)}|[\hat{\mathcal{H}}-E]\bar{\Psi}'^{(\pm)}\rangle_{\mathfrak{V}}\end{aligned} \tag{8.14}$$

[cf. the right side of Eq. (7.4)], the latter become

$$F^{(\pm)}[\mathsf{f}^{(\pm)\dagger},\mathsf{f}'^{(\pm)};\overline{\mathsf{c}}^{(\pm)\dagger},\overline{\mathsf{c}}'^{(\pm)}]=\mathsf{f}^{(\pm)\dagger}\overline{\mathsf{c}}'^{(\pm)}+\overline{\mathsf{c}}^{(\pm)\dagger}\mathsf{f}'^{(\pm)}-\overline{\mathsf{c}}^{(\pm)\dagger}\tilde{\mathsf{S}}^{(\pm)}\overline{\mathsf{c}}'^{(\pm)}, \quad (8.15)$$

where $\mathsf{f}^{(\pm)\dagger}$ and $\overline{\mathsf{c}}^{(\pm)\dagger}$ are row matrices with rank $\mathsf{M}^{(\pm)}$ elements $\{f_n^{(\pm)*}=(\Phi|\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)})_{\mathfrak{S}}\}$ and $\{\overline{c}_n^{(\pm)*}\}$, respectively, $\mathsf{f}'^{(\pm)}$ and $\overline{\mathsf{c}}'^{(\pm)}$ are column matrices with rank $\mathsf{M}^{(\pm)}$ elements $\{f_n'^{(\pm)}=(\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)}|\Phi')_{\mathfrak{S}}\}$ and $\{\overline{c}_n'^{(\pm)}\}$, respectively, while $\tilde{\mathsf{S}}^{(\pm)}(E)$ are rank $\mathsf{M}^{(\pm)}\times$rank $\mathsf{M}^{(\pm)}$ Hermitian matrices with elements

$$\tilde{S}_{nn'}^{(\pm)}(E)=-\gamma^{(\mp)}(\tilde{\Psi}_n^{(\pm)}|i\hat{\mathcal{E}}_{\perp}^{(\pm)}\tilde{\Psi}_{n'}^{(\pm)})_{\mathfrak{S}}-\frac{\gamma^{(\mp)}}{c\hbar}\langle\tilde{\Psi}_n^{(\pm)}|[\hat{\mathcal{H}}-E]\tilde{\Psi}_{n'}^{(\pm)}\rangle_{\mathfrak{V}}. \quad (8.16)$$

These particular vectors $\overline{\mathsf{c}}^{(\pm)\dagger}$ and $\overline{\mathsf{c}}'^{(\pm)}$, which make the functionals (8.15) stationary, will be designated by $\tilde{\mathsf{c}}^{(\pm)\dagger}$ and $\tilde{\mathsf{c}}'^{(\pm)}$, respectively. Performing the first variations of $F^{(\pm)}$ due to small and otherwise arbitrary variations of $\overline{\mathsf{c}}^{(\pm)\dagger}$ and $\overline{\mathsf{c}}'^{(\pm)}$ around $\tilde{\mathsf{c}}^{(\pm)\dagger}$ and $\tilde{\mathsf{c}}'^{(\pm)}$, it is found that sufficient conditions for $F^{(\pm)}$ to be stationary are

$$\tilde{\mathsf{c}}^{(\pm)\dagger}=\mathsf{f}^{(\pm)\dagger}(\tilde{\mathsf{S}}^{(\pm)})^{-1}, \quad \tilde{\mathsf{c}}'^{(\pm)}=(\tilde{\mathsf{S}}^{(\pm)})^{-1}\mathsf{f}'^{(\pm)}. \quad (8.17)$$

Substituting these optimal vectors $\tilde{\mathsf{c}}^{(\pm)\dagger}$ and $\tilde{\mathsf{c}}'^{(\pm)}$ into the functionals (8.15), we obtain the following variational estimates of $(\Phi|\hat{\mathcal{R}}^{(\pm)}\Phi')_{\mathfrak{S}}$:

$$(\Phi|\hat{\tilde{\mathcal{R}}}^{(\pm)}\Phi')_{\mathfrak{S}}=\mathsf{f}^{(\pm)\dagger}(\tilde{\mathsf{S}}^{(\pm)})^{-1}\mathsf{f}'^{(\pm)}=\sum_{n,n'=1}^{\text{rank }\mathsf{M}^{(\pm)}}(\Phi|\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)})_{\mathfrak{S}}\times[(\tilde{\mathsf{S}}^{(\pm)})^{-1}]_{nn'}(\hat{\beta}^{(\pm)}\tilde{\Psi}_{n'}^{(\pm)}|\Phi')_{\mathfrak{S}}. \quad (8.18)$$

Equation (8.18) may be simplified since from the considerations of Sec. VIII A it follows that the matrices $\tilde{\mathsf{S}}^{(\pm)}(E)$ are diagonal and

$$\tilde{S}_{nn'}^{(\pm)}(E)=\widetilde{b_n^{\pm 1}}(E)(\tilde{\Psi}_n^{(\pm)}|\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)})_{\mathfrak{S}}\delta_{nn'}. \quad (8.19)$$

Consequently, Eq. (8.18) becomes

$$(\Phi|\hat{\tilde{\mathcal{R}}}^{(\pm)}\Phi')_{\mathfrak{S}}=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\pm)}}\frac{(\Phi|\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)})_{\mathfrak{S}}\ (\widetilde{b_n^{\pm 1}})^{-1}(\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)}|\Phi')_{\mathfrak{S}}}{(\tilde{\Psi}_n^{(\pm)}|\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)})_{\mathfrak{S}}}. \quad (8.20)$$

Since the hypersurface functions $\Phi(\varrho)$ and $\Phi'(\varrho)$ are arbitrary, Eq. (8.20) defines two linear integral operators $\hat{\tilde{\mathcal{R}}}^{(\pm)}(E)$ with the kernels

$$\tilde{\mathcal{R}}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\pm)}}\frac{\beta_K^{(\pm)}\tilde{\Psi}_n^{(\pm)}(E,\varrho_K)[\widetilde{b_n^{\pm 1}}(E)]^{-1}\tilde{\Psi}_n^{(\pm)\dagger}(E,\varrho'_{K'})\beta_{K'}^{(\pm)}}{(\tilde{\Psi}_n^{(\pm)}|\hat{\beta}^{(\pm)}\tilde{\Psi}_n^{(\pm)})_{\mathfrak{S}}} \quad (8.21)$$

[cf. the spectral expansions (5.6)]. The operators $\hat{\tilde{\mathcal{R}}}^{(\pm)}(E)$ are variational estimates of the operators $\hat{\mathcal{R}}^{(\pm)}(E)$.

C. Estimates of matrix elements and kernels of $\hat{\mathcal{B}}^{(\pm)}(E)$

The approximate eigenfunctions $\{\tilde{\Psi}_n^{(-)}(E,\mathfrak{r})\}$ and $\{\tilde{\Psi}_n^{(+)}(E,\mathfrak{r})\}$ (notice the order) may be employed as basis functions for the variational determination of approximations to matrix elements of the operators $\hat{\mathcal{B}}^{(+)}(E)$ and $\hat{\mathcal{B}}^{(-)}(E)$, respectively. Extremalization of the functionals

$$F^{(\pm)}[\Phi,\Phi';\overline{\Psi}^{(\pm)},\overline{\Psi}'^{(\pm)}]=-\gamma^{(\mp)}(\Phi|i\hat{\mathcal{E}}_{\perp}^{(\pm)}\overline{\Psi}'^{(\pm)})_{\mathfrak{S}}-\gamma^{(\mp)}(i\hat{\mathcal{E}}_{\perp}^{(\pm)}\overline{\Psi}^{(\pm)}|\Phi')_{\mathfrak{S}}+\gamma^{(\mp)}(i\hat{\mathcal{E}}_{\perp}^{(\pm)}\overline{\Psi}^{(\pm)}|\overline{\Psi}'^{(\pm)})_{\mathfrak{S}}-\frac{\gamma^{(\mp)}}{c\hbar}\langle\overline{\Psi}^{(\pm)}|[\hat{\mathcal{H}}-E]\overline{\Psi}'^{(\pm)}\rangle_{\mathfrak{V}} \quad (8.22)$$

[cf. the variational principles (7.2)] in the class of trial functions

$$\overline{\Psi}^{(\pm)}(\mathfrak{r})=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\mp)}}\overline{c}_n^{(\pm)}\tilde{\Psi}_n^{(\mp)}(E,\mathfrak{r}),$$
$$\overline{\Psi}'^{(\pm)}(\mathfrak{r})=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\mp)}}\overline{c}_n'^{(\pm)}\tilde{\Psi}_n^{(\mp)}(E,\mathfrak{r}) \quad (8.23)$$

[notice the difference between Eqs. (8.13) and (8.23)] yields the following estimates of the matrix elements $(\Phi|\hat{\mathcal{B}}^{(\pm)}\Phi')_{\mathfrak{S}}$:

$$(\Phi|\hat{\tilde{\mathcal{B}}}^{(\pm)}\Phi')=(\gamma^{(\mp)})^2\sum_{n,n'=1}^{\text{rank }\mathsf{M}^{(\mp)}}(\Phi|i\hat{\mathcal{E}}_{\perp}^{(\pm)}\tilde{\Psi}_n^{(\mp)})_{\mathfrak{S}}\times[(\tilde{\mathsf{T}}^{(\pm)})^{-1}]_{nn'}(i\hat{\mathcal{E}}_{\perp}^{(\pm)}\tilde{\Psi}_{n'}^{(\mp)}|\Phi')_{\mathfrak{S}}, \quad (8.24)$$

where $\tilde{\mathsf{T}}^{(\pm)}(E)$ are rank $\mathsf{M}^{(\mp)}\times$rank $\mathsf{M}^{(\mp)}$ Hermitian matrices with elements

$$\tilde{T}^{(\pm)}_{nn'}(E)=-\gamma^{(\mp)}(i\hat{\mathcal{E}}^{(\pm)}_{\perp}\tilde{\Psi}^{(\mp)}_{n}|\tilde{\Psi}^{(\mp)}_{n'})_{\mathfrak{S}}+\frac{\gamma^{(\mp)}}{c\hbar}\langle\tilde{\Psi}^{(\mp)}_{n}|[\hat{\mathcal{H}}-E]\tilde{\Psi}^{(\mp)}_{n'}\rangle_{\mathfrak{V}}. \tag{8.25}$$

A glance at Eqs. (8.16) and (8.25) (and comparison of matrix dimensions) shows that elements of the matrices $\tilde{\mathsf{T}}^{(\pm)}(E)$ are simply related to elements of the diagonal matrices $\tilde{\mathsf{S}}^{(\mp)}(E)$ introduced in Sec. VIII B:

$$\tilde{T}^{(\pm)}_{nn'}(E)=(\gamma^{(\mp)})^2\tilde{S}^{(\mp)}_{nn'}(E). \tag{8.26}$$

Hence and from Eq. (8.19) one infers that

$$\tilde{T}^{(\pm)}_{nn'}(E)=(\gamma^{(\mp)})^2\widetilde{b^{\mp 1}_{n}}(E)(\tilde{\Psi}^{(\mp)}_{n}|\hat{\beta}^{(\mp)}\tilde{\Psi}^{(\mp)}_{n})_{\mathfrak{S}}\delta_{nn'} \tag{8.27}$$

and consequently the estimates (8.24) become

$$(\Phi|\hat{\tilde{\mathcal{B}}}^{(\pm)}\Phi')_{\mathfrak{S}}=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\mp)}}\frac{(\Phi|i\hat{\mathcal{E}}^{(\pm)}_{\perp}\tilde{\Psi}^{(\mp)}_{n})_{\mathfrak{S}}(\widetilde{b^{\mp 1}_{n}})^{-1}(i\hat{\mathcal{E}}^{(\pm)}_{\perp}\tilde{\Psi}^{(\mp)}_{n}|\Phi')_{\mathfrak{S}}}{(\tilde{\Psi}^{(\mp)}_{n}|\hat{\beta}^{(\mp)}\tilde{\Psi}^{(\mp)}_{n})_{\mathfrak{S}}}. \tag{8.28}$$

Equation (8.28) defines two linear integral operators $\hat{\tilde{\mathcal{B}}}^{(\pm)}(E)$ with the kernels

$$\tilde{\mathcal{B}}^{(\pm)}(E,\varrho_K,\varrho'_{K'})=\sum_{n=1}^{\text{rank }\mathsf{M}^{(\mp)}}\frac{\text{æ}^{(\pm)}_{\perp K}(\varrho_K)\tilde{\Psi}^{(\mp)}_{n}(E,\varrho_K)[\widetilde{b^{\mp 1}_{n}}(E)]^{-1}\tilde{\Psi}^{(\mp)\dagger}_{n}(E,\varrho'_{K'})\text{æ}^{(\mp)}_{\perp K'}(\varrho'_{K'})}{(\tilde{\Psi}^{(\mp)}_{n}|\hat{\beta}^{(\mp)}\tilde{\Psi}^{(\mp)}_{n})_{\mathfrak{S}}} \tag{8.29}$$

[cf. the expansions (4.14)]. These operators are variational estimates of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$.

IX. MULTICONFIGURATION DIRAC-HARTREE-FOCK APPROACH TO THE *R*-MATRIX METHOD FOR RELATIVISTIC MANY-ELECTRON SYSTEMS

It is evident that the success of the method, presented in Sec. VIII A and aimed at approximating eigenvalues and eigenfunctions of $\hat{\mathcal{B}}^{(\pm)}(E)$ [and $\hat{\mathcal{R}}^{(\mp)}(E)$] with the use of the linear trial functions (8.1), depends greatly on the right choice of the basis functions $\{\Theta_i(\mathfrak{r})\}$. All premises (in particular, any known symmetries of the system) should be exploited to obtain converged results with a variational basis of the size as small as possible. Difficulties that may be encountered in the course of achieving this goal, due to the stiffness of the basis functions used, may be, at least partly, overcome within the framework of the multiconfiguration Dirac-Hartree-Fock *R*-matrix approach proposed below. This method is an extension of the nonrelativistic Hartree-Fock *R*-matrix method suggested about a decade ago by Hinze and Hamacher [24,25] and elaborated on recently by the author [17].

We begin with introducing μ one-electron four-component spin orbitals $\{\overline{\psi}_{\nu}(\mathbf{r})\}$ *without* prescribing their forms and subjecting them only to the orthonormality constraints within the volume $\mathcal{V}$:

$$\langle\overline{\psi}_{\nu}|\overline{\psi}_{\eta}\rangle=\delta_{\nu\eta}. \tag{9.1}$$

From Kronecker's products of these spin orbitals, making use of the antisymmetrizer $\hat{\mathcal{A}}_{\mathfrak{V}}$, we may construct $\mu_N=\binom{\mu}{N}$ *different* N-electron Slater determinants

$$\begin{aligned}\overline{\Theta}_i(\mathfrak{r})&\equiv\overline{\Theta}_{\iota_1\iota_2\cdots\iota_N}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\\&=\sqrt{N!}\,\hat{\mathcal{A}}_{\mathfrak{V}}\{\overline{\psi}_{\iota_1}(\mathbf{r}_1)\otimes\overline{\psi}_{\iota_2}(\mathbf{r}_2)\otimes\cdots\otimes\overline{\psi}_{\iota_N}(\mathbf{r}_N)\}\\&=\frac{1}{\sqrt{N!}}\det|\overline{\psi}_{\iota_1}(\mathbf{r}_1),\overline{\psi}_{\iota_2}(\mathbf{r}_2),\ldots,\overline{\psi}_{\iota_N}(\mathbf{r}_N)|\end{aligned} \tag{9.2}$$

with $\iota_1<\iota_2<\cdots<\iota_N$ to avoid redundancy. The functions $\{\overline{\Theta}_i(\mathfrak{r})\}$ obtained in that way are mutually orthonormal:

$$\langle\overline{\Theta}_i|\overline{\Theta}_n\rangle_{\mathfrak{V}}=\delta_{in}, \tag{9.3}$$

where $i=\{\iota_1\iota_2\cdots\iota_N\}$, $n=\{\nu_1\nu_2\cdots\nu_N\}$, and

$$\delta_{in}=\delta_{\iota_1\nu_1}\delta_{\iota_2\nu_2}\cdots\delta_{\iota_N\nu_N}. \tag{9.4}$$

Then, from the set $\{\overline{\Theta}_i(\mathfrak{r})\}$ we choose $m\leqslant\mu_N$ elements and form the trial function

$$\overline{\Psi}(\mathfrak{r})=\sum_{i=1}^{m}\overline{a}_i\overline{\Theta}_i(\mathfrak{r}), \tag{9.5}$$

which is to be used in the functionals

$$F^{(\pm)}[\overline{\Psi},\{\overline{\lambda}_{\nu\eta}\}]=-\gamma^{(\mp)}\frac{(\overline{\Psi}|i\hat{\mathcal{E}}^{(\pm)}_{\perp}\overline{\Psi})_{\mathfrak{S}}}{(\overline{\Psi}|\hat{\beta}^{(\pm)}\overline{\Psi})_{\mathfrak{S}}}-\frac{\gamma^{(\mp)}}{c\hbar}\frac{\langle\overline{\Psi}|[\hat{\mathcal{H}}-E]\overline{\Psi}\rangle_{\mathfrak{V}}}{(\overline{\Psi}|\hat{\beta}^{(\pm)}\overline{\Psi})_{\mathfrak{S}}}+\frac{\sum_{\nu,\eta=1}^{\mu}\overline{\lambda}_{\nu\eta}[\langle\overline{\psi}_{\nu}|\overline{\psi}_{\eta}\rangle-\delta_{\nu\eta}]}{(\overline{\Psi}|\hat{\beta}^{(\pm)}\overline{\Psi})_{\mathfrak{S}}} \tag{9.6}$$

for variational optimization of approximations to the eigenvalues $\{b^{\pm 1}(E)\}$. The functionals (9.6) differ from Eq. (8.2) since in the current approach we have to take into account the orthonormality constraints (9.1); this has been done including the last term on the right-hand side of Eq. (9.6) in which $\{\overline{\lambda}_{\nu\eta}\}$ are the Lagrange multipliers, optimal values of which are to be determined simultaneously with the optimal values of the coefficients $\{\overline{a}_i\}$ and the optimal forms of the spin orbitals $\{\overline{\psi}_\nu(\mathbf{r})\}$.

Before we apply the variational principle to the functionals (9.6), we reduce them to the forms containing $\{\overline{a}_i\}$, $\{\overline{\psi}_\nu(\mathbf{r})\}$, and their conjugates explicitly. This is most conveniently done with the aid of the annihilation operators defined so that [26]

$$\hat{A}_\nu \overline{\Theta}^{(N)}_{\{\iota_1\iota_2\cdots\iota_N\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)=\begin{cases}(-)^{N+j}\overline{\Theta}^{(N-1)}_{\{\iota_1\iota_2\cdots\iota_{j-1}\iota_{j+1}\cdots\iota_N\}}(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N-1}) & \text{for } \nu=\iota_j\in\{\iota_1,\iota_2,\ldots,\iota_N\}\\ 0 \quad \text{for } \nu\notin\{\iota_1,\iota_2,\ldots,\iota_N\}\end{cases}, \tag{9.7}$$

where the superscripts in the parentheses at the Θ's refer to the numbers of electrons described by these functions. The annihilators defined in that way anticommute

$$\hat{A}_\nu\hat{A}_\eta+\hat{A}_\eta\hat{A}_\nu=0 \tag{9.8}$$

and with the aid of them the Slater determinants (9.2) may be rewritten equivalently as

$$\overline{\Theta}_i(\mathfrak{r})=\frac{1}{\sqrt{N}}\sum_{\nu=1}^{\mu}[\hat{A}_\nu\overline{\Theta}_i(\mathfrak{r})]\otimes\overline{\psi}_\nu(\mathbf{r}_N)=\frac{1}{\sqrt{N(N-1)}}\sum_{\nu,\eta=1}^{\mu}[\hat{A}_\nu\hat{A}_\eta\overline{\Theta}_i(\mathfrak{r})]\otimes\overline{\psi}_\nu(\mathbf{r}_{N-1})\otimes\overline{\psi}_\eta(\mathbf{r}_N). \tag{9.9}$$

Using Eqs. (9.1)–(9.9), the functionals (9.6) become

$$\begin{aligned}F^{(\pm)}[\{\overline{a}_i^*\},\{\overline{a}_i\},\{\overline{\psi}_\nu^\dagger\},\{\overline{\psi}_\nu\},\{\overline{\varepsilon}^{(\pm)}_{\nu\eta}\}]=&-\gamma^{(\mp)}\frac{\sum_{i,j=1}^{m}\overline{a}_i^*\overline{a}_j\sum_{\nu,\eta=1}^{\mu}\omega^{(ij)}_{\nu\eta}(\overline{\psi}_\nu|i\alpha_\perp^{(\pm)}\overline{\psi}_\eta)}{\sum_{i,j=1}^{m}\overline{a}_i^*\overline{a}_j\sum_{\nu,\eta=1}^{\mu}\omega^{(ij)}_{\nu\eta}(\overline{\psi}_\nu|\beta^{(\pm)}\overline{\psi}_\eta)}\\ &-\frac{\gamma^{(\mp)}}{c\hbar}\frac{\sum_{i,j=1}^{m}\overline{a}_i^*\overline{a}_j\left[\sum_{\nu,\eta=1}^{\mu}\left(\omega^{(ij)}_{\nu\eta}\langle\overline{\psi}_\nu|\hat{H}\overline{\psi}_\eta\rangle+\frac{1}{2}\sum_{\xi,\zeta=1}^{\mu}\Omega^{(ij)}_{\nu\xi,\eta\zeta}\langle\overline{\psi}_\nu\overline{\psi}_\xi|U\overline{\psi}_\eta\overline{\psi}_\zeta\rangle_{v\times v}\right)-E\delta_{ij}\right]}{\sum_{i,j=1}^{m}\overline{a}_i^*\overline{a}_j\sum_{\nu,\eta=1}^{\mu}\omega^{(ij)}_{\nu\eta}(\overline{\psi}_\nu|\beta^{(\pm)}\overline{\psi}_\eta)}\\ &+\frac{\gamma^{(\mp)}}{c\hbar}\frac{\sum_{\nu,\eta=1}^{\mu}\overline{\varepsilon}^{(\pm)}_{\nu\eta}[\langle\overline{\psi}_\nu|\overline{\psi}_\eta\rangle-\delta_{\nu\eta}]}{\sum_{i,j=1}^{m}\overline{a}_i^*\overline{a}_j\sum_{\nu,\eta=1}^{\mu}\omega^{(ij)}_{\nu\eta}(\overline{\psi}_\nu|\beta^{(\pm)}\overline{\psi}_\eta)},\end{aligned} \tag{9.10}$$

where, for the sake of convenience, we have replaced the Lagrange multipliers $\{\overline{\lambda}_{\nu\eta}\}$ by the related multipliers

$$\overline{\varepsilon}^{(\pm)}_{\nu\eta}=-c\hbar\,\gamma^{(\pm)}\overline{\lambda}_{\nu\eta} \tag{9.11}$$

and defined the coefficients

$$\omega^{(ij)}_{\nu\eta}=\langle\hat{A}_\nu\overline{\Theta}_i|\hat{A}_\eta\overline{\Theta}_j\rangle_{\mathcal{V}^{N-1}}=\begin{cases}\pm 1 & \text{if } \nu\in i \text{ and } \eta\in j\\ 0 & \text{otherwise}\end{cases}, \tag{9.12}$$

$$\begin{aligned}\Omega^{(ij)}_{\nu\xi,\eta\zeta}=&\langle\hat{A}_\nu\hat{A}_\xi\overline{\Theta}_i|\hat{A}_\eta\hat{A}_\zeta\overline{\Theta}_j\rangle_{\mathcal{V}^{N-2}}\\ =&\begin{cases}\pm 1 & \text{if } \nu,\xi\in i \text{ and } \eta,\zeta\in j\\ 0 & \text{otherwise}\end{cases}.\end{aligned} \tag{9.13}$$

The stationary values of the functionals (9.10) approximate eigenvalues of the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\mp)}(E)$; the best estimates are given by

$$\widetilde{b^{\pm 1}}=F^{(\pm)}[\{\tilde{a}_i^{(\pm)*}\},\{\tilde{a}_i^{(\pm)}\},\{\tilde{\psi}_\nu^{(\pm)\dagger}\},\{\tilde{\psi}_\nu^{(\pm)}\},\{\tilde{\varepsilon}^{(\pm)}_{\nu\eta}\}], \tag{9.14}$$

where the optimal expansion coefficients $\{\tilde{a}_i^{(\pm)}\}$, spin orbitals $\{\tilde{\psi}_\nu^{(\pm)}(\mathbf{r})\}$, their conjugates as well as the Lagrange multipliers $\{\tilde{\varepsilon}^{(\pm)}_{\nu\eta}\}$ are determined from the stationarity condition

$$\delta F^{(\pm)}[\{\tilde{a}_i^{(\pm)*}\},\{\tilde{a}_i^{(\pm)}\},\{\tilde{\psi}_\nu^{(\pm)\dagger}\},\{\overline{\psi}_\nu^{(\pm)}\},\{\tilde{\varepsilon}^{(\pm)}_{\nu\eta}\}]=0. \tag{9.15}$$

Varying the functionals in Eq. (9.10) and applying the condition (9.15), one obtains a set of finite-volume multiconfiguration Dirac-Hartree-Fock *R*-matrix equations comprising the generalized algebraic eigenproblem

$$\sum_{j=1}^{m} [\tilde{S}_{ij}^{(\pm)} - \widetilde{b^{\pm 1}} \tilde{M}_{ij}^{(\pm)}] \tilde{a}_j^{(\pm)} = 0 \tag{9.16}$$

with

$$\tilde{S}_{ij}^{(\pm)} = -\gamma^{(\mp)} \sum_{\nu,\eta=1}^{\mu} \omega_{\nu\eta}^{(ij)} (\tilde{\psi}_\nu^{(\pm)} | i\alpha_\perp^{(\pm)} \tilde{\psi}_\eta^{(\pm)}) - \frac{\gamma^{(\mp)}}{c\hbar} \sum_{\nu,\eta=1}^{\mu} \left[\omega_{\nu\eta}^{(ij)} \langle \tilde{\psi}_\nu^{(\pm)} | \hat{H} \tilde{\psi}_\eta^{(\pm)} \rangle + \tfrac{1}{2} \sum_{\xi,\zeta=1}^{\mu} \Omega_{\nu\xi,\eta\zeta}^{(ij)} \times \langle \tilde{\psi}_\nu^{(\pm)} \tilde{\psi}_\xi^{(\pm)} | U \tilde{\psi}_\eta^{(\pm)} \tilde{\psi}_\zeta^{(\pm)} \rangle_{\mathcal{V}\times\mathcal{V}} \right] + \frac{\gamma^{(\mp)}}{c\hbar} E \delta_{ij} \tag{9.17}$$

and

$$\tilde{M}_{ij}^{(\pm)} = \sum_{\nu,\eta=1}^{\mu} \omega_{\nu\eta}^{(ij)} (\tilde{\psi}_\nu^{(\pm)} | \beta^{(\pm)} \tilde{\psi}_\eta^{(\pm)}), \tag{9.18}$$

and the coupled integro-differential equations

$$\sum_{\eta=1}^{\mu} \tilde{\omega}_{\nu\eta}^{(\pm)} \hat{H}(\mathbf{r}) \tilde{\psi}_\eta^{(\pm)}(\mathbf{r}) + \sum_{\eta,\xi,\zeta=1}^{\mu} \tilde{\Omega}_{\nu\xi,\eta\zeta}^{(\pm)} \langle \tilde{\psi}_\xi^{(\pm)} | U \tilde{\psi}_\zeta^{(\pm)} \rangle \tilde{\psi}_\eta^{(\pm)}(\mathbf{r}) = \sum_{\eta=1}^{\mu} \tilde{\varepsilon}_{\nu\eta}^{(\pm)} \tilde{\psi}_\eta^{(\pm)}(\mathbf{r}), \tag{9.19}$$

solutions of which are subjected to the boundary conditions

$$\sum_{\eta=1}^{\mu} \tilde{\omega}_{\nu\eta}^{(\pm)} [i\alpha_\perp^{(\pm)}(\boldsymbol{\rho}) \tilde{\psi}_\eta^{(\pm)}(\boldsymbol{\rho}) - \gamma^{(\pm)} \widetilde{b^{\pm 1}} \beta^{(\pm)} \tilde{\psi}_\eta^{(\pm)}(\boldsymbol{\rho})] = 0. \tag{9.20}$$

One obtains also a set of conjugated equations

$$\sum_{i=1}^{m} \tilde{a}_i^{(\pm)*} [\tilde{S}_{ij}^{(\pm)} - \widetilde{b^{\pm 1}} \tilde{M}_{ij}^{(\pm)}] = 0, \tag{9.21}$$

$$\sum_{\nu=1}^{\mu} \tilde{\omega}_{\nu\eta}^{(\pm)} [\hat{H}(\mathbf{r}) \tilde{\psi}_\nu^{(\pm)}(\mathbf{r})]^\dagger + \sum_{\nu,\xi,\zeta=1}^{\mu} \tilde{\Omega}_{\nu\xi,\eta\zeta}^{(\pm)} \tilde{\psi}_\nu^{(\pm)\dagger}(\mathbf{r}) \langle \tilde{\psi}_\xi^{(\pm)} | U \tilde{\psi}_\zeta^{(\pm)} \rangle = \sum_{\nu=1}^{\mu} \tilde{\varepsilon}_{\nu\eta}^{(\pm)} \tilde{\psi}_\nu^{(\pm)\dagger}(\mathbf{r}), \tag{9.22}$$

$$\sum_{\nu=1}^{\mu} \tilde{\omega}_{\nu\eta}^{(\pm)} [[i\alpha_\perp^{(\pm)}(\boldsymbol{\rho}) \tilde{\psi}_\nu^{(\pm)}(\boldsymbol{\rho})]^\dagger - \gamma^{(\pm)} \widetilde{b^{\pm 1}} [\beta^{(\pm)} \tilde{\psi}_\nu^{(\pm)}(\boldsymbol{\rho})]^\dagger] = 0. \tag{9.23}$$

In addition, the orthonormality constraints

$$\langle \tilde{\psi}_\nu^{(\pm)} | \tilde{\psi}_\eta^{(\pm)} \rangle = \delta_{\nu\eta} \tag{9.24}$$

follow in agreement with Eq. (9.1). The quantities $\{\tilde{\omega}_{\nu\eta}^{(\pm)}\}$ and $\{\tilde{\Omega}_{\nu\xi,\eta\zeta}^{(\pm)}\}$ appearing in the above equations are defined by

$$\tilde{\omega}_{\nu\eta}^{(\pm)} = \sum_{i,j=1}^{m} \tilde{a}_i^{(\pm)*} \omega_{\nu\eta}^{(ij)} \tilde{a}_j^{(\pm)}, \qquad \tilde{\Omega}_{\nu\xi,\eta\zeta}^{(\pm)} = \sum_{i,j=1}^{m} \tilde{a}_i^{(\pm)*} \Omega_{\nu\xi,\eta\zeta}^{(ij)} \tilde{a}_j^{(\pm)}. \tag{9.25}$$

From Eqs. (9.19) and (9.22), with the aid of the orthonormality relations (9.24), one derives

$$\tilde{\varepsilon}_{\nu\eta}^{(\pm)} = \sum_{\sigma=1}^{\mu} \tilde{\omega}_{\nu\sigma}^{(\pm)} \langle \tilde{\psi}_\eta^{(\pm)} | \hat{H} \tilde{\psi}_\sigma^{(\pm)} \rangle + \sum_{\sigma,\xi,\zeta=1}^{\mu} \tilde{\Omega}_{\nu\xi,\sigma\zeta}^{(\pm)} \times \langle \tilde{\psi}_\eta^{(\pm)} \tilde{\psi}_\xi^{(\pm)} | U \tilde{\psi}_\sigma^{(\pm)} \tilde{\psi}_\zeta^{(\pm)} \rangle_{\mathcal{V}\times\mathcal{V}} \tag{9.26}$$

and

$$\tilde{\varepsilon}_{\nu\eta}^{(\pm)} = \sum_{\sigma=1}^{\mu} \tilde{\omega}_{\sigma\eta}^{(\pm)} \langle \hat{H} \tilde{\psi}_\sigma^{(\pm)} | \tilde{\psi}_\nu^{(\pm)} \rangle + \sum_{\sigma,\xi,\zeta=1}^{\mu} \tilde{\Omega}_{\sigma\xi,\eta\zeta}^{(\pm)} \times \langle \tilde{\psi}_\sigma^{(\pm)} \tilde{\psi}_\xi^{(\pm)} | U \tilde{\psi}_\nu^{(\pm)} \tilde{\psi}_\zeta^{(\pm)} \rangle_{\mathcal{V}\times\mathcal{V}}, \tag{9.27}$$

hence one immediately infers that

$$\tilde{\varepsilon}_{\nu\eta}^{(\pm)} = \tilde{\varepsilon}_{\eta\nu}^{(\pm)*}, \tag{9.28}$$

i.e., matrices composed of the Lagrange multipliers are Hermitian.

The multiconfiguration Dirac-Hartree-Fock (MCDHF) *R*-matrix equations (9.16), (9.19), and (9.20) are to be solved self-consistently. In this context, several features that distinguish these equations from standard MCDHF problems encountered in computations of atomic structures [27–35] are to be emphasized. First, in the present case we have a finite-volume problem, since the system is considered within the volume $\mathcal{V}$. Second, the total energy of the system E is now prescribed; instead, boundary conditions obeyed by the spin orbitals on the surface $\mathcal{S}$ enclosing $\mathcal{V}$ are *not* known in advance (as opposed to the case of the standard MCDHF problems, in which the spin orbitals are forced to vanish at the boundary located at infinity) but are to be determined in the course of solving the equations. And third, in the algebraic systems (9.16) the weight matrices $\tilde{\mathbf{M}}^{(\pm)}$ with the elements $\tilde{M}_{ij}^{(\pm)}$ are highly singular and special numerical algorithms, for instance the QZ algorithm [36,37], for solving such systems have to be employed.

We conclude this section stressing that Eqs. (9.16), (9.19), and (9.20) provide *two*, in general *different*, sets of the MCDHF *R*-matrix equations, depending on which superscripts, upper or lower, are chosen. Results obtained by solving these sets of equations will be, in general, different as long as the number of spin orbitals optimized is finite (which is always the case in actual computations). A difference between results obtained in the two cases may serve as an additional criterion of the accuracy of the method.

X. CONCLUSIONS

In this work we have attempted to present a unified approach to the variational *R*-matrix methods for many-electron relativistic systems. The approach has been based on the operator formulation of the relativistic *R*-matrix theory, in which central objects are the integral operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$ [38]. We have presented a set of variational principles for eigenvalues and matrix elements of these operators. Utilizing these principles with the Rayleigh-Ritz linear trial functions, we have obtained suitable variational estimates of eigenvalues, matrix elements, and kernels of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$. Finally, we have proposed the multiconfiguration Dirac-Hartree-Fock approach to the *R*-matrix method for many-electron systems. We write a computer code implementing that approach.

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