

The finite-volume Dirac–Hartree–Fock method for confined relativistic many-electron systems

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Abstract

An energy eigenproblem for a relativistic N -electron system confined to the interior of a finite volume \mathcal{V} is considered. The confinement is modelled by imposing a local impedance boundary condition at a hypersurface enclosing the hypervolume \mathcal{V}^N in the configuration space. It is shown that energy eigenvalues are non-increasing functions of the hypersurface impedance. Variational principles for energy eigenvalues, admitting the use of trial functions which do not obey the boundary condition imposed on exact eigenfunctions, are constructed in a systematic manner. The Dirac–Hartree–Fock method is applied to derive integro-differential equations and local boundary conditions satisfied by one-electron spin orbitals from which the best determinantal approximations to exact eigenfunctions are built. It is proved that the Dirac–Hartree–Fock estimates of exact energy eigenvalues are also non-increasing functions of the hypersurface impedance.

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1. Introduction

The recent two decades have seen a growth of interest in the theory of confined many-electron atomic and molecular systems [1]. Browsing the literature on the subject, one finds that nearly all relevant papers report results obtained within the framework of non-relativistic quantum mechanics. The exceptions are recent papers by Connerade *et al* [2–5]. These authors studied numerically ground-state properties of many-electron atoms confined in spherical cavities in

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the Dirac–Hartree–Fock (DHF) approach; the confinement was modelled by introducing a very high, but still finite, repulsive potential barrier into the radial DHF equations.

In this paper we investigate mathematical properties of a model of confinement differing from the one adopted in [2–5]. Specifically, we consider an energy eigenproblem for a relativistic N -electron system (e.g., an electronic cloud of an atom or a molecule, or a group of electrons in a solid) confined to the interior of a finite, in general non-spherical, volume $\mathcal{V} \subset \mathbb{R}^3$. The configuration space for this system is the hypervolume \mathcal{V}^N and the N -electron Dirac equation describing the system is considered in this hypervolume. To accomplish the confinement, and to provide the data necessary to set up an energy eigenproblem, we impose a local boundary condition on solutions to this Dirac equation at a hypersurface enclosing the hypervolume \mathcal{V}^N . This boundary condition contains a free real parameter, which may be identified with the hypersurface impedance, and we show that energy levels of the confined system are non-increasing functions of this parameter.

In the theory of unconfined relativistic many-electron systems the DHF approximation has been proved to be extremely useful. Therefore, the idea to apply this approximation to the model of confinement defined above is very appealing. We show that this idea is realizable but with much more effort than for unconfined systems. Complications arise from the fact that the standard variational principle for energy eigenvalues of unconfined systems, from which, after necessary modifications, unconfined DHF equations for optimal one-electron spin orbitals are usually derived, presupposes a *vanishing* boundary condition at *infinity* and therefore cannot be simply adapted to the present *finite-volume* model with the *impedance* boundary condition. To avoid this difficulty, we employ the procedure popularized by Gerjuoy *et al* [6] and construct two variational principles for energy eigenvalues of the problem at hand. After modifying these principles, in order to obtain ones suitable for use with the determinantal trial functions built of orthonormal trial spin orbitals, we derive finite-volume DHF equations obeyed in \mathcal{V} by optimal spin orbitals (these equations appear to be formally identical with the DHF equations for unconfined systems) *and* boundary conditions satisfied by these spin orbitals at a surface enclosing \mathcal{V} . Employing properties of solutions to the resulting DHF eigenproblem, we prove that DHF estimates of energy levels of the confined system possess the same property as exact total eigenenergies, i.e., are non-increasing functions of the impedance parameter.

2. 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} , its position vector will be marked with $\boldsymbol{\rho}$. A unit outward vector normal to \mathcal{S} at the point $\boldsymbol{\rho}$ will be denoted by $\mathbf{n}(\boldsymbol{\rho})$.

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

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

and

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

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 the N -fold Cartesian product of \mathcal{V} :

$$\mathfrak{V} = \mathcal{V}^N \equiv \mathcal{V}_1 \times \cdots \times \mathcal{V}_N, \tag{2.3}$$

bounded by a hypersurface

$$\mathfrak{S} = \bigcup_{K=1}^N \mathfrak{S}_K \tag{2.4}$$

composed of N geometrically similar hyperfacets, with the K th hyperfacet defined as

$$\mathfrak{S}_K = \mathcal{V}_1 \times \cdots \times \mathcal{V}_{K-1} \times \mathcal{S}_K \times \mathcal{V}_{K+1} \times \cdots \times \mathcal{V}_N \quad (K = 1, 2, \dots, N). \tag{2.5}$$

A position vector of a point in the hypervolume \mathfrak{V} will be denoted by \mathbf{r} . If the point \mathbf{r} lies on \mathfrak{S} , we shall denote this using the symbol ϱ instead of \mathbf{r} . If we wish to emphasize that the point ϱ is on the particular hyperfacet \mathfrak{S}_K , we shall indicate this adding the subscript K at ϱ , i.e., writing ϱ_K instead of ϱ . A unit outward vector normal to \mathfrak{S} at the point ϱ will be denoted by $\mathbf{n}(\varrho)$.

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

$$\langle \Phi | \Phi' \rangle_{\mathfrak{V}} \equiv \int_{\mathfrak{V}} d^{3N} \mathbf{r} \Phi^\dagger(\mathbf{r}) \Phi'(\mathbf{r}) \tag{2.6}$$

and

$$\langle \Phi | \Phi' \rangle_{\mathfrak{S}} \equiv \oint_{\mathfrak{S}} d^{3N-1} \varrho \Phi^\dagger(\varrho) \Phi'(\varrho), \tag{2.7}$$

respectively. Here $d^{3N} \mathbf{r}$ denotes an infinitesimal element of the hypervolume \mathfrak{V} around the point \mathbf{r} and $d^{3N-1} \varrho$ is an infinitesimal *scalar* element of the hypersurface \mathfrak{S} around the point ϱ .

3. Model of confinement

Consider a relativistic N -electron system confined in the physical space to an interior of a finite volume $\mathcal{V} \subset \mathbb{R}^3$ enclosed by a sufficiently smooth, connected surface \mathcal{S} . Then, a configuration point \mathbf{r} of the system is confined to an interior of the finite hypervolume $\mathfrak{V} \subset \mathbb{R}^{3N}$, defined in equation (2.3), enclosed by the hypersurface \mathfrak{S} defined in equations (2.4), (2.5). The time-independent Dirac equation describing the electrons in a stationary state of total energy E (including electrons' rest energies), represented by a 4^N -component spinor $\Psi(\mathbf{r})$, is

$$[\hat{\mathcal{H}} - E]\Psi(\mathbf{r}) = 0 \quad (\mathbf{r} \in \mathfrak{V}), \tag{3.1}$$

with the Hamiltonian

$$\hat{\mathcal{H}} = \sum_{K=1}^N [-ic\hbar \mathbf{A}_K \cdot \nabla_K + \beta_K mc^2 + V(\mathbf{r}_K)] + \frac{1}{2} \sum_{\substack{K, K'=1 \\ (K \neq K')}}^N U(\mathbf{r}_K, \mathbf{r}_{K'}). \tag{3.2}$$

Here ∇_K is the gradient operator with respect to coordinates of the K th electron, \mathbf{A}_K and β_K are $4^N \times 4^N$ matrices defined as the following tensor products:

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

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

with α and β denoting the standard Dirac matrices [7] and \mathcal{I} denoting the unit 4×4 matrix. For later convenience, we observe that Hamiltonian (3.2) may be rewritten in the form

$$\hat{\mathcal{H}} = -ic\hbar\mathbf{A}\cdot\mathfrak{D} + \sum_{K=1}^N [\beta_K mc^2 + V(\mathbf{r}_K)] + \frac{1}{2} \sum_{\substack{K,K'=1 \\ (K \neq K')}}^N U(\mathbf{r}_K, \mathbf{r}_{K'}), \quad (3.5)$$

where

$$\mathfrak{D} = [\nabla_1, \dots, \nabla_N], \quad (3.6)$$

$$\mathbf{A} = [\mathbf{A}_1, \dots, \mathbf{A}_N]. \quad (3.7)$$

In equations (3.2) and (3.5), $V(\mathbf{r}_K)$ and $U(\mathbf{r}_K, \mathbf{r}_{K'}) = U(\mathbf{r}_{K'}, \mathbf{r}_K)$ are real, local, one- and two-electron potentials, respectively.

We shall model the confinement of the system by imposing the following boundary condition on $\Psi(\mathbf{r})$ at the hypersurface \mathfrak{S} :

$$[i\hat{\mathbf{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathbf{b}}^{(\pm)}] \Psi(\varrho) = 0 \quad (\varrho \in \mathfrak{S}). \quad (3.8)$$

(It will be proved in appendix B that both possible choices of superscripts lead to *the same* boundary condition.) In equation (3.8), b is a real prescribed constant (hypersurface impedance), the constants $\gamma^{(\pm)}$ are defined as

$$\gamma^{(\pm)} = -(\gamma^{(\mp)})^{-1} = \pm \left(\frac{\hbar}{2mc} \right)^{\pm 1}, \quad (3.9)$$

and $\hat{\mathbf{b}}^{(\pm)}$ is an operator such that for any 4^N -component spinor function $\Phi(\varrho)$ defined on \mathfrak{S} it holds

$$\hat{\mathbf{b}}^{(\pm)} \Phi(\varrho_K) = \beta_K^{(\pm)} \Phi(\varrho_K), \quad (3.10)$$

where

$$\beta_K^{(\pm)} = \mathcal{I}_1 \otimes \dots \otimes \mathcal{I}_{K-1} \otimes \beta_K^{(\pm)} \otimes \mathcal{I}_{K+1} \otimes \dots \otimes \mathcal{I}_N, \quad (3.11)$$

with

$$\beta^{(\pm)} = \frac{1}{2} [\mathcal{I} \pm \beta]. \quad (3.12)$$

Moreover, we define

$$\hat{\mathbf{A}}_{\perp}^{(\pm)} = \hat{\mathbf{b}}^{(\pm)} \hat{\mathbf{A}}_{\perp}, \quad (3.13)$$

where $\hat{\mathbf{A}}_{\perp}$ is a hypersurface integral operator with the kernel

$$\mathbf{A}_{\perp}(\varrho, \varrho') = \mathbf{n}(\varrho) \cdot \mathbf{A} \delta^{(3N-1)}(\varrho - \varrho') \quad (3.14)$$

and $\delta^{(3N-1)}(\varrho - \varrho')$ is the Dirac delta function on the hypersurface \mathfrak{S} . (Some useful properties of the operators $\hat{\mathbf{A}}_{\perp}^{(\pm)}$ and $\hat{\mathbf{b}}^{(\pm)}$ have been collected in appendix A.)

4. General properties of the energy eigenvalue E

From the defining equations (3.1) and (3.8) one may draw conclusions about the reality of the energy eigenvalue E and about the dependence of the latter on the impedance parameter b .

To prove the reality of E , we observe that equation (3.1) implies

$$\langle \Psi | \hat{\mathcal{H}} \Psi \rangle_{\mathfrak{S}} - \langle \hat{\mathcal{H}} \Psi | \Psi \rangle_{\mathfrak{S}} = [E - E^*] \langle \Psi | \Psi \rangle_{\mathfrak{S}}. \quad (4.1)$$

On the other hand, exploiting the $3N$ -dimensional Gauss integration theorem we have

$$\langle \Psi | \hat{\mathcal{H}} \Psi \rangle_{\mathfrak{Y}} - \langle \hat{\mathcal{H}} \Psi | \Psi \rangle_{\mathfrak{Y}} = -c\hbar \langle \Psi | i\hat{\mathcal{E}}_{\perp} \Psi \rangle_{\mathfrak{S}} \tag{4.2}$$

and further, after transforming the right-hand side of equation (4.2) with the aid of equation (A.1) and the first of equations (A.6),

$$\langle \Psi | \hat{\mathcal{H}} \Psi \rangle_{\mathfrak{Y}} - \langle \hat{\mathcal{H}} \Psi | \Psi \rangle_{\mathfrak{Y}} = -c\hbar \langle \Psi | i\hat{\mathcal{E}}_{\perp}^{(\pm)} \Psi \rangle_{\mathfrak{S}} + c\hbar \langle i\hat{\mathcal{E}}_{\perp}^{(\pm)} \Psi | \Psi \rangle_{\mathfrak{S}}. \tag{4.3}$$

Applying the boundary condition (3.8) to the right-hand side of equation (4.3), making use of the reality of b and of the second of equations (A.6), we arrive at

$$\langle \Psi | \hat{\mathcal{H}} \Psi \rangle_{\mathfrak{Y}} - \langle \hat{\mathcal{H}} \Psi | \Psi \rangle_{\mathfrak{Y}} = 0. \tag{4.4}$$

Combining equations (4.1) and (4.4), we conclude that the energy eigenvalue E is real.

To investigate the dependence of E on b , we differentiate the Dirac equation (3.1) with respect to $b^{\pm 1}$. After rearrangement, this yields

$$\frac{\partial E}{\partial b^{\pm 1}} \Psi(\mathbf{r}) = [\hat{\mathcal{H}} - E] \frac{\partial \Psi(\mathbf{r})}{\partial b^{\pm 1}} \quad (\mathbf{r} \in \mathfrak{Y}), \tag{4.5}$$

hence, one has

$$\frac{\partial E}{\partial b^{\pm 1}} \langle \Psi | \Psi \rangle_{\mathfrak{Y}} = \left\langle \Psi \left| [\hat{\mathcal{H}} - E] \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{Y}} \right\rangle. \tag{4.6}$$

Next, transforming the right-hand side of equation (4.6) with the aid of the $3N$ -dimensional Gauss integration theorem and exploiting the reality of E gives

$$\frac{\partial E}{\partial b^{\pm 1}} \langle \Psi | \Psi \rangle_{\mathfrak{Y}} = \left\langle [\hat{\mathcal{H}} - E] \Psi \left| \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{Y}} \right\rangle - c\hbar \left\langle \Psi \left| i\hat{\mathcal{E}}_{\perp} \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{S}} \right\rangle, \tag{4.7}$$

which, in virtue of equation (3.1), simplifies to

$$\frac{\partial E}{\partial b^{\pm 1}} \langle \Psi | \Psi \rangle_{\mathfrak{Y}} = -c\hbar \left\langle \Psi \left| i\hat{\mathcal{E}}_{\perp} \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{S}} \right\rangle. \tag{4.8}$$

Application of equation (A.1) and the first of equations (A.6) leads to

$$\frac{\partial E}{\partial b^{\pm 1}} \langle \Psi | \Psi \rangle_{\mathfrak{Y}} = -c\hbar \left\langle \Psi \left| i\hat{\mathcal{E}}_{\perp}^{(\pm)} \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{S}} \right\rangle + c\hbar \left\langle i\hat{\mathcal{E}}_{\perp}^{(\pm)} \Psi \left| \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{S}} \right\rangle. \tag{4.9}$$

Hence, after making use of the boundary condition (3.8) and of the second of equations (A.6), we have

$$\frac{\partial E}{\partial b^{\pm 1}} \langle \Psi | \Psi \rangle_{\mathfrak{Y}} = -c\hbar \left\langle \Psi \left| [i\hat{\mathcal{E}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \frac{\partial \Psi}{\partial b^{\pm 1}} \right|_{\mathfrak{S}} \right\rangle. \tag{4.10}$$

Finally, after employing the relationship

$$[i\hat{\mathcal{E}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \frac{\partial \Psi(\boldsymbol{\varrho})}{\partial b^{\pm 1}} = \gamma^{(\pm)} \hat{\beta}^{(\pm)} \Psi(\boldsymbol{\varrho}) \quad (\boldsymbol{\varrho} \in \mathfrak{S}), \tag{4.11}$$

obtained after differentiating the boundary condition (3.8) with respect to $b^{\pm 1}$, we arrive at

$$\frac{\partial E}{\partial b^{\pm 1}} = -c\hbar \gamma^{(\pm)} \frac{\langle \Psi | \hat{\beta}^{(\pm)} \Psi \rangle_{\mathfrak{S}}}{\langle \Psi | \Psi \rangle_{\mathfrak{Y}}}. \tag{4.12}$$

Since the matrix element $\langle \Psi | \hat{\beta}^{(+)} \Psi \rangle_{\mathfrak{S}}$ is non-negative, invoking equation (3.9) one infers that

$$\frac{\partial E}{\partial b} \leq 0, \tag{4.13}$$

i.e., E is a non-increasing function of b .

5. Construction of variational principles for the energy eigenvalue E

In this section, it will be our goal to *construct*, employing the recipe presented by Gerjuoy *et al* [6], variational principles equivalent to the eigenproblem (3.1) and (3.8).

Following [6], we shall seek two functionals $\mathcal{F}^{(\pm)}$ in the form

$$\mathcal{F}^{(\pm)}[\bar{E}, \bar{\Psi}; \bar{\Lambda}^{(\pm)}, \bar{\lambda}^{(\pm)}] = \bar{E} + \langle \bar{\Lambda}^{(\pm)} | [\hat{\mathcal{H}} - \bar{E}] \bar{\Psi} \rangle_{\mathfrak{Y}} + \langle \bar{\lambda}^{(\pm)} | [i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)}] \bar{\Psi} \rangle_{\mathfrak{S}}, \quad (5.1)$$

where \bar{E} is a trial eigenenergy, $\bar{\Psi}(\mathbf{r})$ is a trial eigenfunction, while $\bar{\Lambda}^{(\pm)}(\mathbf{r})$ and $\bar{\lambda}^{(\pm)}(\varrho)$ are Lagrange functions, undetermined at this stage, introduced to incorporate equations (3.1) and (3.8) as constraints. The functionals (5.1) possess the property

$$\mathcal{F}^{(\pm)}[E, \Psi; \bar{\Lambda}^{(\pm)}, \bar{\lambda}^{(\pm)}] = E \quad (5.2)$$

for any choices of $\bar{\Lambda}^{(\pm)}(\mathbf{r})$ and $\bar{\lambda}^{(\pm)}(\varrho)$.

The first variations of $\mathcal{F}^{(\pm)}$, due to variations in \bar{E} , $\bar{\Psi}(\mathbf{r})$, $\bar{\Lambda}^{(\pm)}(\mathbf{r})$ and $\bar{\lambda}^{(\pm)}(\varrho)$ around E , $\Psi(\mathbf{r})$, $\Lambda^{(\pm)}(\mathbf{r})$ and $\lambda^{(\pm)}(\varrho)$, respectively, where $\Lambda^{(\pm)}(\mathbf{r})$ and $\lambda^{(\pm)}(\varrho)$ are some, so far arbitrary, functions, are

$$\begin{aligned} \delta\mathcal{F}^{(\pm)}[E, \Psi; \Lambda^{(\pm)}, \lambda^{(\pm)}] &= \delta E + \langle \delta\Lambda^{(\pm)} | [\hat{\mathcal{H}} - E] \Psi \rangle_{\mathfrak{Y}} - \delta E \langle \Lambda^{(\pm)} | \Psi \rangle_{\mathfrak{Y}} \\ &+ \langle \Lambda^{(\pm)} | [\hat{\mathcal{H}} - E] \delta\Psi \rangle_{\mathfrak{Y}} + (\delta\lambda^{(\pm)} | [i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)}] \Psi)_{\mathfrak{S}} \\ &+ (\lambda^{(\pm)} | [i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)}] \delta\Psi)_{\mathfrak{S}}. \end{aligned} \quad (5.3)$$

In virtue of equations (3.1) and (3.8), the second and the fifth terms on the right-hand side of equation (5.3) vanish. Next, employing the $3N$ -dimensional Gauss integration theorem in the fourth term on the right-hand side of equation (5.3) yields

$$\begin{aligned} \delta\mathcal{F}^{(\pm)}[E, \Psi; \Lambda^{(\pm)}, \lambda^{(\pm)}] &= \delta E [1 - \langle \Lambda^{(\pm)} | \Psi \rangle_{\mathfrak{Y}}] + \langle [\hat{\mathcal{H}} - E] \Lambda^{(\pm)} | \delta\Psi \rangle_{\mathfrak{Y}} \\ &- (\Lambda^{(\pm)} | i\hbar\hat{\mathcal{A}}_{\perp} \delta\Psi)_{\mathfrak{S}} + (\lambda^{(\pm)} | [i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)}] \delta\Psi)_{\mathfrak{S}}. \end{aligned} \quad (5.4)$$

Since the operators $\hat{\mathcal{A}}_{\perp}^{(\pm)}$ and $\hat{\mathcal{B}}^{(\pm)}$ possess the properties (A.6) and since b is real, equation (5.4) may be rewritten in the form

$$\begin{aligned} \delta\mathcal{F}^{(\pm)}[E, \Psi; \Lambda^{(\pm)}, \lambda^{(\pm)}] &= \delta E [1 - \langle \Lambda^{(\pm)} | \Psi \rangle_{\mathfrak{Y}}] + \langle [\hat{\mathcal{H}} - E] \Lambda^{(\pm)} | \delta\Psi \rangle_{\mathfrak{Y}} \\ &+ (i\hbar\hat{\mathcal{A}}_{\perp} \Lambda^{(\pm)} + [-i\hat{\mathcal{A}}_{\perp}^{(\mp)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)}] \lambda^{(\pm)} | \delta\Psi)_{\mathfrak{S}}. \end{aligned} \quad (5.5)$$

We shall choose the functions $\Lambda^{(\pm)}(\mathbf{r})$ and $\lambda^{(\pm)}(\varrho)$ so that

$$\delta\mathcal{F}^{(\pm)}[E, \Psi; \Lambda^{(\pm)}, \lambda^{(\pm)}] = 0. \quad (5.6)$$

It is evident from equation (5.5) that this stationarity condition will be satisfied if $\Lambda^{(\pm)}(\mathbf{r})$ and $\lambda^{(\pm)}(\varrho)$ are such that

$$1 - \langle \Lambda^{(\pm)} | \Psi \rangle_{\mathfrak{Y}} = 0, \quad (5.7)$$

$$[\hat{\mathcal{H}} - E] \Lambda^{(\pm)}(\mathbf{r}) = 0 \quad (\mathbf{r} \in \mathfrak{Y}), \quad (5.8)$$

$$i\hbar\hat{\mathcal{A}}_{\perp} \Lambda^{(\pm)}(\varrho) - i\hat{\mathcal{A}}_{\perp}^{(\mp)} \lambda^{(\pm)}(\varrho) - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)} \lambda^{(\pm)}(\varrho) = 0 \quad (\varrho \in \mathfrak{S}). \quad (5.9)$$

Operating on equation (5.9) from the left either with $\hat{\mathcal{B}}^{(\pm)}$ or with $\hat{\mathcal{B}}^{(\mp)}$, and then making use of equations (A.2)–(A.5) yields

$$i\hbar\hat{\mathcal{A}}_{\perp}^{(\pm)} \Lambda^{(\pm)}(\varrho) - \gamma^{(\pm)} b^{\pm 1} \hat{\mathcal{B}}^{(\pm)} \lambda^{(\pm)}(\varrho) = 0 \quad (\varrho \in \mathfrak{S}) \quad (5.10)$$

or

$$i\hbar\hat{\mathcal{A}}_{\perp}^{(\mp)} \Lambda^{(\pm)}(\varrho) - i\hat{\mathcal{A}}_{\perp}^{(\mp)} \lambda^{(\pm)}(\varrho) = 0 \quad (\varrho \in \mathfrak{S}), \quad (5.11)$$

respectively. Acting then on equation (5.11) from the left with $\hat{A}_\perp^{(\pm)}$ and employing equation (A.3), we find

$$\hat{\beta}^{(\pm)}\lambda^{(\pm)}(\varrho) = c\hbar\hat{\beta}^{(\pm)}\Lambda^{(\pm)}(\varrho) \quad (\varrho \in \mathfrak{S}). \tag{5.12}$$

Inserting equation (5.12) into equation (5.10) gives

$$i\hat{A}_\perp^{(\pm)}\Lambda^{(\pm)}(\varrho) - \gamma^{(\pm)}b^{\pm 1}\hat{\beta}^{(\pm)}\Lambda^{(\pm)}(\varrho) = 0 \quad (\varrho \in \mathfrak{S}). \tag{5.13}$$

From equations (5.8) and (5.13), it is evident that the functions $\Lambda^{(\pm)}(\mathbf{r})$ satisfy the same Dirac equation in \mathfrak{Y} and the same boundary condition on \mathfrak{S} as $\Psi(\mathbf{r})$. Hence, it follows that we may choose

$$\Lambda^{(\pm)}(\mathbf{r}) = \eta^{(\pm)}\Psi(\mathbf{r}) \quad (\mathbf{r} \in \mathfrak{Y}), \tag{5.14}$$

where $\eta^{(\pm)}$ are some complex numbers. To determine $\eta^{(\pm)}$, we substitute equation (5.14) into equation (5.9), which gives

$$\eta^{(\pm)} = \frac{1}{\langle \Psi | \Psi \rangle_{\mathfrak{Y}}}. \tag{5.15}$$

From this and from equations (5.14) and (5.12) we obtain the following relationships:

$$\Lambda^{(\pm)}(\mathbf{r}) = \frac{1}{\langle \Psi | \Psi \rangle_{\mathfrak{Y}}} \Psi(\mathbf{r}) \quad (\mathbf{r} \in \mathfrak{Y}), \tag{5.16}$$

$$\hat{\beta}^{(\pm)}\lambda^{(\pm)}(\varrho) = \frac{c\hbar}{\langle \Psi | \Psi \rangle_{\mathfrak{Y}}} \hat{\beta}^{(\pm)}\Psi(\varrho) \quad (\varrho \in \mathfrak{S}). \tag{5.17}$$

Equations (5.16) and (5.17) suggest the following choices of the trial Lagrange functions $\bar{\Lambda}^{(\pm)}(\mathbf{r})$ and $\bar{\lambda}^{(\pm)}(\varrho)$ in the starting functional (5.1):

$$\bar{\Lambda}^{(\pm)}(\mathbf{r}) = \frac{1}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}} \bar{\Psi}(\mathbf{r}) \quad (\mathbf{r} \in \mathfrak{Y}), \tag{5.18}$$

$$\hat{\beta}^{(\pm)}\bar{\lambda}^{(\pm)}(\varrho) = \frac{c\hbar}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}} \hat{\beta}^{(\pm)}\bar{\Psi}(\varrho) \quad (\varrho \in \mathfrak{S}). \tag{5.19}$$

Taking then into account that

$$(\bar{\lambda}^{(\pm)} | [i\hat{A}_\perp^{(\pm)} - \gamma^{(\pm)}b^{\pm 1}\hat{\beta}^{(\pm)}] \bar{\Psi})_{\mathfrak{S}} = (\hat{\beta}^{(\pm)}\bar{\lambda}^{(\pm)} | [i\hat{A}_\perp^{(\pm)} - \gamma^{(\pm)}b^{\pm 1}\hat{\beta}^{(\pm)}] \bar{\Psi})_{\mathfrak{S}} \tag{5.20}$$

and employing relations (A.2) and (A.5), we arrive at the functionals

$$\mathcal{F}^{(\pm)}[\bar{\Psi}] = \frac{\langle \bar{\Psi} | \hat{\mathcal{H}} \bar{\Psi} \rangle_{\mathfrak{Y}}}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}} + c\hbar \frac{(\bar{\Psi} | [i\hat{A}_\perp^{(\pm)} - \gamma^{(\pm)}b^{\pm 1}\hat{\beta}^{(\pm)}] \bar{\Psi})_{\mathfrak{S}}}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}}. \tag{5.21}$$

From equations (5.21), (5.6) and (5.2) we have the variational principles

$$\delta\mathcal{F}^{(\pm)}[\bar{\Psi}] = 0 \quad E = \mathcal{F}^{(\pm)}[\bar{\Psi}], \tag{5.22}$$

equivalent to the eigenproblem (3.1) and (3.8).

The functionals (5.21) possess the useful property of assuming real values for an arbitrary trial function $\bar{\Psi}(\mathbf{r})$. Indeed, with the aid of the $3N$ -dimensional Gauss integration theorem the complex conjugate of equation (5.21),

$$\mathcal{F}^{(\pm)*}[\bar{\Psi}] = \frac{\langle \hat{\mathcal{H}} \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}} + c\hbar \frac{([i\hat{A}_\perp^{(\pm)} - \gamma^{(\pm)}b^{\pm 1}\hat{\beta}^{(\pm)}] \bar{\Psi} | \bar{\Psi})_{\mathfrak{S}}}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{Y}}}, \tag{5.23}$$

may be transformed to the form

$$\mathcal{F}^{(\pm)*}[\bar{\Psi}] = \frac{\langle \bar{\Psi} | \hat{\mathcal{H}} \bar{\Psi} \rangle_{\mathfrak{D}}}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{D}}} + c\hbar \frac{(\bar{\Psi} | i\hat{\mathcal{A}}_{\perp} \bar{\Psi})_{\mathfrak{S}} + ([i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \bar{\Psi} | \bar{\Psi})_{\mathfrak{S}}}{\langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{D}}}. \quad (5.24)$$

Further, from the fact that b is real and from equations (A.6) one has

$$([i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \bar{\Psi} | \bar{\Psi})_{\mathfrak{S}} = (\bar{\Psi} | [-i\hat{\mathcal{A}}_{\perp}^{(\mp)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \bar{\Psi})_{\mathfrak{S}}. \quad (5.25)$$

Substituting this into equation (5.24) and employing relation (A.1), we find that the right-hand side of the resulting equation is identical with the right-hand side of equation (5.21), which implies that $\mathcal{F}^{(\pm)}[\bar{\Psi}]$ are real.

Above, in the considerations leading to the functionals (5.21), we have not assumed normalization of the exact eigenfunction $\Psi(\mathbf{r})$. If, however, we impose the constraint

$$\langle \Psi | \Psi \rangle_{\mathfrak{D}} - 1 = 0, \quad (5.26)$$

equations (5.16) and (5.17) become

$$\Lambda^{(\pm)}(\mathbf{r}) = \Psi(\mathbf{r}) \quad (\mathbf{r} \in \mathfrak{D}) \quad (5.27)$$

and

$$\hat{\beta}^{(\pm)} \lambda^{(\pm)}(\varrho) = c\hbar \hat{\beta}^{(\pm)} \Psi(\varrho) \quad (\varrho \in \mathfrak{S}), \quad (5.28)$$

respectively. If we choose $\bar{\Lambda}^{(\pm)}(\mathbf{r})$ and $\bar{\lambda}^{(\pm)}(\varrho)$ to be related to $\bar{\Psi}(\mathbf{r})$ and $\bar{\Psi}(\varrho)$ in the analogous way, i.e.,

$$\bar{\Lambda}^{(\pm)}(\mathbf{r}) = \bar{\Psi}(\mathbf{r}) \quad (\mathbf{r} \in \mathfrak{D}), \quad (5.29)$$

$$\hat{\beta}^{(\pm)} \bar{\lambda}^{(\pm)}(\varrho) = c\hbar \hat{\beta}^{(\pm)} \bar{\Psi}(\varrho) \quad (\varrho \in \mathfrak{S}), \quad (5.30)$$

then, instead of the functionals (5.21), we get

$$\mathcal{F}^{(\pm)}[\bar{E}, \bar{\Psi}] = \langle \bar{\Psi} | \hat{\mathcal{H}} \bar{\Psi} \rangle_{\mathfrak{D}} + c\hbar (\bar{\Psi} | [i\hat{\mathcal{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \bar{\Psi})_{\mathfrak{S}} + \bar{E}[1 - \langle \bar{\Psi} | \bar{\Psi} \rangle_{\mathfrak{D}}]. \quad (5.31)$$

(We emphasize that, despite constraint (5.26), analogous normalization of $\bar{\Psi}(\mathbf{r})$ is *not* required.) From equations (5.31), (5.6) and (5.2) we have the variational principles

$$\delta \mathcal{F}^{(\pm)}[E, \Psi] = 0, \quad E = \mathcal{F}^{(\pm)}[E, \Psi], \quad (5.32)$$

equivalent to the eigenproblem (3.1) and (3.8), provided eigenfunctions of this eigenproblem are normalized to unity. A reasoning, analogous to that presented above for the functionals (5.21), may be carried out to show that the functionals (5.31) are real for arbitrary trial functions *provided the estimate \bar{E} is real*.

Two remarks are in order here. First, the functionals (5.21) and (5.31) differ from those used for unconfined systems in that the latter do not contain terms with hypersurface integrals over \mathfrak{S} . In general, in the functionals (5.21) and (5.31) the surface terms will vanish only if the trial function $\bar{\Psi}(\mathbf{r})$ is constrained to obey the boundary condition (3.8). Second, it should be emphasized that although the functionals $\mathcal{F}^{(+)}[\bar{\Psi}]$ and $\mathcal{F}^{(-)}[\bar{\Psi}]$ have the same stationary values (which are energy eigenvalues of the eigensystem (3.1) and (3.8)), they differ one from the other and for an arbitrary $\bar{\Psi}(\mathbf{r})$ one has, in general, $\mathcal{F}^{(+)}[\bar{\Psi}] \neq \mathcal{F}^{(-)}[\bar{\Psi}]$. The second remark applies to the pair of the functionals $\mathcal{F}^{(\pm)}[\bar{E}, \bar{\Psi}]$ as well.

For the purposes of this work, the variational principles (5.31) are more suitable than (5.21). In the next section we shall use their modified versions to determine approximate solutions to the eigensystem (3.1) and (3.8).

6. The Dirac–Hartree–Fock method for confined systems

In this section, we shall use the Dirac–Hartree–Fock (DHF) approach to find approximations to eigensolutions of the system (3.1) and (3.8). To this end, we shall approximate the eigenfunction $\Psi(\mathbf{r})$ by Slater determinants

$$\overline{\Psi}_{\text{DHF}}^{(\pm)}(\mathbf{r}) = \frac{1}{\sqrt{N!}} \sum_{k_1=1}^N \cdots \sum_{k_N=1}^N \epsilon_{k_1 \cdots k_N} \overline{\psi}_{k_1}^{(\pm)}(\mathbf{r}_1) \otimes \cdots \otimes \overline{\psi}_{k_N}^{(\pm)}(\mathbf{r}_N) \quad (\mathbf{r} \in \mathfrak{V}) \quad (6.1)$$

($\epsilon_{k_1 \cdots k_N}$ is the Levi-Civita completely antisymmetric symbol), built of one-electron four-component spinors $\{\overline{\psi}_k^{(\pm)}(\mathbf{r})\}$, which are orthonormal in the sense of

$$\langle \overline{\psi}_k^{(\pm)} | \overline{\psi}_{k'}^{(\pm)} \rangle = \delta_{kk'}. \quad (6.2)$$

The orthonormality conditions (6.2) imply

$$\langle \overline{\Psi}_{\text{DHF}}^{(\pm)} | \overline{\Psi}_{\text{DHF}}^{(\pm)} \rangle_{\mathfrak{V}} = 1. \quad (6.3)$$

To determine the optimal forms of $\{\overline{\psi}_k^{(\pm)}(\mathbf{r})\}$, denoted hereafter as $\{\psi_k^{(\pm)}(\mathbf{r})\}$, and to find the optimal estimates $E_{\text{DHF}}^{(\pm)}$ of E , we shall employ the variational principles

$$\delta \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\psi_k^{(\pm)}\}, \{\varepsilon_{kk'}^{(\pm)}\}] = 0, \quad E_{\text{DHF}}^{(\pm)} = \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\psi_k^{(\pm)}\}, \{\varepsilon_{kk'}^{(\pm)}\}], \quad (6.4)$$

with the functionals

$$\begin{aligned} \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\psi_k^{(\pm)}\}, \{\varepsilon_{kk'}^{(\pm)}\}] &= \langle \overline{\Psi}_{\text{DHF}}^{(\pm)} | \hat{\mathcal{H}} \overline{\Psi}_{\text{DHF}}^{(\pm)} \rangle_{\mathfrak{V}} + c\hbar \langle \overline{\Psi}_{\text{DHF}}^{(\pm)} | [i\hat{A}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\mathbf{B}}^{(\pm)}] \overline{\Psi}_{\text{DHF}}^{(\pm)} \rangle_{\mathfrak{E}} \\ &+ \sum_{k,k'=1}^N \overline{\varepsilon}_{k'k}^{(\pm)} [\delta_{kk'} - \langle \overline{\psi}_k^{(\pm)} | \overline{\psi}_{k'}^{(\pm)} \rangle]. \end{aligned} \quad (6.5)$$

These functionals are formally obtained from the functionals (5.31) by employing equation (6.3) and introducing the term containing the Lagrange multipliers $\{\overline{\varepsilon}_{kk'}^{(\pm)}\}$, incorporating the orthonormality constraints (6.2). The optimal multipliers $\{\varepsilon_{kk'}^{(\pm)}\}$ have to be determined simultaneously with $\{\psi_k^{(\pm)}(\mathbf{r})\}$.

It should be emphasized that since the two functionals $\mathcal{F}_{\text{DHF}}^{(\pm)}$ defined in equation (6.5) differ, at this stage one has to admit the possibility that the extremalization of $\mathcal{F}_{\text{DHF}}^{(+)}$ may yield the spin orbitals $\{\psi_k^{(+)}(\mathbf{r})\}$, the Lagrange multipliers $\{\varepsilon_{kk'}^{(+)}\}$ and the approximate total energy eigenvalue $E_{\text{DHF}}^{(+)}$ differing from $\{\psi_k^{(-)}(\mathbf{r})\}$, $\{\varepsilon_{kk'}^{(-)}\}$ and $E_{\text{DHF}}^{(-)}$ obtained from the extremalization of $\mathcal{F}_{\text{DHF}}^{(-)}$. We shall return to this point later in this section.

Standard manipulations with determinantal functions yield

$$\langle \overline{\Psi}_{\text{DHF}}^{(\pm)} | \hat{\mathcal{H}} \overline{\Psi}_{\text{DHF}}^{(\pm)} \rangle_{\mathfrak{V}} = \sum_{k=1}^N \langle \overline{\psi}_k^{(\pm)} | \hat{H} \overline{\psi}_k^{(\pm)} \rangle + \frac{1}{2} \sum_{k,k'=1}^N \langle \langle \overline{\psi}_k^{(\pm)} \overline{\psi}_{k'}^{(\pm)} | U [1 - \hat{P}_{kk'}] \overline{\psi}_k^{(\pm)} \overline{\psi}_{k'}^{(\pm)} \rangle \rangle, \quad (6.6)$$

where

$$\hat{H} = -i\hbar\boldsymbol{\alpha} \cdot \nabla + \beta mc^2 + V(\mathbf{r}), \quad (6.7)$$

$$\langle \langle \overline{\psi}_a^{(\pm)} \overline{\psi}_b^{(\pm)} | U \overline{\psi}_c^{(\pm)} \overline{\psi}_d^{(\pm)} \rangle \rangle = \int_{\mathfrak{V}} d^3\mathbf{r} \int_{\mathfrak{V}} d^3\mathbf{r}' \overline{\psi}_a^{(\pm)\dagger}(\mathbf{r}) \otimes \overline{\psi}_b^{(\pm)\dagger}(\mathbf{r}') U(\mathbf{r}, \mathbf{r}') \overline{\psi}_c^{(\pm)}(\mathbf{r}) \otimes \overline{\psi}_d^{(\pm)}(\mathbf{r}'), \quad (6.8)$$

and $\hat{P}_{kk'}$ is the operator interchanging the indices k and k' . Further, the reasoning

presented in appendix C gives

$$(\overline{\Psi}_{\text{DHF}}^{(\pm)} | [\mathbf{i}\hat{\mathbf{A}}_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \hat{\beta}^{(\pm)}] \overline{\Psi}_{\text{DHF}}^{(\pm)})_{\mathfrak{S}} = \sum_{k=1}^N (\overline{\psi}_k^{(\pm)} | [\mathbf{i}\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \overline{\psi}_k^{(\pm)}), \quad (6.9)$$

where

$$\alpha_{\perp}^{(\pm)}(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho}) \cdot \beta^{(\pm)} \boldsymbol{\alpha}. \quad (6.10)$$

This allows us to express the functionals (6.5) explicitly in terms of the spin orbitals $\{\overline{\psi}_k^{(\pm)}(\mathbf{r})\}$:

$$\begin{aligned} \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\overline{\psi}_k^{(\pm)}\}, \{\overline{\varepsilon}_{kk'}^{(\pm)}\}] &= \sum_{k=1}^N \langle \overline{\psi}_k^{(\pm)} | \hat{H} \overline{\psi}_k^{(\pm)} \rangle + c\hbar \sum_{k=1}^N (\overline{\psi}_k^{(\pm)} | [\mathbf{i}\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \overline{\psi}_k^{(\pm)}) \\ &+ \frac{1}{2} \sum_{k,k'=1}^N \langle \overline{\psi}_k^{(\pm)} \overline{\psi}_{k'}^{(\pm)} | U[1 - \hat{P}_{kk'}] \overline{\psi}_k^{(\pm)} \overline{\psi}_{k'}^{(\pm)} \rangle + \sum_{k,k'=1}^N \overline{\varepsilon}_{k'k}^{(\pm)} [\delta_{kk'} - \langle \overline{\psi}_k^{(\pm)} | \overline{\psi}_{k'}^{(\pm)} \rangle]. \end{aligned} \quad (6.11)$$

The first variations of the functionals (6.11) due to variations in $\{\overline{\psi}_k^{(\pm)}(\mathbf{r})\}$, $\{\overline{\psi}_k^{(\pm)}(\boldsymbol{\rho})\}$ and $\{\overline{\varepsilon}_{kk'}^{(\pm)}\}$ around $\{\psi_k^{(\pm)}(\mathbf{r})\}$, $\{\psi_k^{(\pm)}(\boldsymbol{\rho})\}$ and $\{\varepsilon_{kk'}^{(\pm)}\}$, respectively, are

$$\begin{aligned} \delta \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\psi_k^{(\pm)}\}, \{\varepsilon_{kk'}^{(\pm)}\}] &= \sum_{k=1}^N \langle \delta \psi_k^{(\pm)} | \hat{H} \psi_k^{(\pm)} \rangle + \sum_{k=1}^N \langle \psi_k^{(\pm)} | \hat{H} \delta \psi_k^{(\pm)} \rangle \\ &+ c\hbar \sum_{k=1}^N (\delta \psi_k^{(\pm)} | [\mathbf{i}\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \psi_k^{(\pm)}) \\ &+ c\hbar \sum_{k=1}^N (\psi_k^{(\pm)} | [\mathbf{i}\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \delta \psi_k^{(\pm)}) \\ &+ \sum_{k,k'=1}^N \langle \delta \psi_k^{(\pm)} \psi_{k'}^{(\pm)} | U[1 - \hat{P}_{kk'}] \psi_k^{(\pm)} \psi_{k'}^{(\pm)} \rangle \\ &+ \sum_{k,k'=1}^N \langle \psi_k^{(\pm)} \psi_{k'}^{(\pm)} | U[1 - \hat{P}_{kk'}] \delta \psi_k^{(\pm)} \psi_{k'}^{(\pm)} \rangle \\ &+ \sum_{k,k'=1}^N \delta \varepsilon_{k'k}^{(\pm)} [\delta_{kk'} - \langle \psi_k^{(\pm)} | \psi_{k'}^{(\pm)} \rangle] \\ &- \sum_{k,k'=1}^N \varepsilon_{k'k}^{(\pm)} [\langle \delta \psi_k^{(\pm)} | \psi_{k'}^{(\pm)} \rangle + \langle \psi_k^{(\pm)} | \delta \psi_{k'}^{(\pm)} \rangle]. \end{aligned} \quad (6.12)$$

Since

$$\alpha_{\perp}^{(\pm)\dagger}(\boldsymbol{\rho}) = \alpha_{\perp}^{(\mp)}(\boldsymbol{\rho}), \quad \beta^{(\pm)\dagger} = \beta^{(\pm)}, \quad (6.13)$$

we have

$$(\psi_k^{(\pm)} | [\mathbf{i}\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \delta \psi_k^{(\pm)}) = ([-\mathbf{i}\alpha_{\perp}^{(\mp)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \psi_k^{(\pm)} | \delta \psi_k^{(\pm)}). \quad (6.14)$$

Further, on applying the three-dimensional Gauss integration theorem, we have

$$(\psi_k^{(\pm)} | \hat{H} \delta \psi_k^{(\pm)}) = \langle \hat{H} \psi_k^{(\pm)} | \delta \psi_k^{(\pm)} \rangle + c\hbar (\mathbf{i}\alpha_{\perp} \psi_k^{(\pm)} | \delta \psi_k^{(\pm)}), \quad (6.15)$$

where

$$\alpha_{\perp}(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho}) \cdot \boldsymbol{\alpha}. \quad (6.16)$$

Combining equations (6.14) and (6.15) with the relationship

$$\alpha_{\perp}(\boldsymbol{\rho}) = \alpha_{\perp}^{(\pm)}(\boldsymbol{\rho}) + \alpha_{\perp}^{(\mp)}(\boldsymbol{\rho}), \quad (6.17)$$

transforms equation (6.12) to the following more suitable form:

$$\begin{aligned} \delta \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\psi_k^{(\pm)}\}, \{\varepsilon_{kk'}^{(\pm)}\}] &= \sum_{k=1}^N \left\langle \delta \psi_k^{(\pm)} \left| \hat{F}^{(\pm)} \psi_k^{(\pm)} - \sum_{k'=1}^N \varepsilon_{k'k}^{(\pm)} \psi_{k'}^{(\pm)} \right. \right\rangle \\ &+ c\hbar \sum_{k=1}^N (\delta \psi_k^{(\pm)} | [i\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \psi_k^{(\pm)}) \\ &+ \sum_{k=1}^N \left\langle \hat{F}^{(\pm)} \psi_k^{(\pm)} - \sum_{k'=1}^N \varepsilon_{kk'}^{(\pm)*} \psi_{k'}^{(\pm)} \left| \delta \psi_k^{(\pm)} \right. \right\rangle \\ &+ c\hbar \sum_{k=1}^N ([i\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \psi_k^{(\pm)} | \delta \psi_k^{(\pm)}) \\ &+ \sum_{k,k'=1}^N \delta \varepsilon_{k'k}^{(\pm)} [\delta_{kk'} - \langle \psi_k^{(\pm)} | \psi_{k'}^{(\pm)} \rangle], \end{aligned} \quad (6.18)$$

with the DHF operators defined as

$$\hat{F}^{(\pm)} = \hat{H} + \sum_{k=1}^N [(\psi_k^{(\pm)} | U \psi_k^{(\pm)}) - |\psi_k^{(\pm)}\rangle U \langle \psi_k^{(\pm)}|]. \quad (6.19)$$

The stationarity condition for $\mathcal{F}_{\text{DHF}}^{(\pm)}$, imposed in equation (6.4), will be satisfied if in equation (6.18) the terms multiplying $\{\delta \psi_k^{(\pm)\dagger}(\mathbf{r})\}$, $\{\delta \psi_k^{(\pm)}(\mathbf{r})\}$, $\{\delta \psi_k^{(\pm)\dagger}(\boldsymbol{\rho})\}$, $\{\delta \psi_k^{(\pm)}(\boldsymbol{\rho})\}$ and $\{\delta \varepsilon_{k'k}^{(\pm)}\}$ vanish separately. On equating to zero terms multiplying $\{\delta \psi_k^{(\pm)\dagger}(\mathbf{r})\}$ and $\{\delta \psi_k^{(\pm)}(\mathbf{r})\}$ in the volume integrals in equation (6.8), we obtain the DHF equations

$$\hat{F}^{(\pm)} \psi_k^{(\pm)}(\mathbf{r}) - \sum_{k'=1}^N \varepsilon_{k'k}^{(\pm)} \psi_{k'}^{(\pm)}(\mathbf{r}) = 0 \quad (\mathbf{r} \in \mathcal{V}) \quad (6.20)$$

and

$$\hat{F}^{(\pm)} \psi_k^{(\pm)}(\mathbf{r}) - \sum_{k'=1}^N \varepsilon_{kk'}^{(\pm)*} \psi_{k'}^{(\pm)}(\mathbf{r}) = 0 \quad (\mathbf{r} \in \mathcal{V}), \quad (6.21)$$

respectively. Further, equating to zero terms multiplying $\{\delta \psi_k^{(\pm)\dagger}(\boldsymbol{\rho})\}$ and $\{\delta \psi_k^{(\pm)}(\boldsymbol{\rho})\}$ in the surface integrals in equation (6.18) yields in both cases the same boundary conditions

$$[i\alpha_{\perp}^{(\pm)}(\boldsymbol{\rho}) - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \psi_k^{(\pm)}(\boldsymbol{\rho}) = 0 \quad (\boldsymbol{\rho} \in \mathcal{S}). \quad (6.22)$$

Finally, equating to zero terms at $\{\delta \varepsilon_{k'k}^{(\pm)}\}$ gives the orthonormality constraints

$$\langle \psi_k^{(\pm)} | \psi_{k'}^{(\pm)} \rangle = \delta_{kk'}, \quad (6.23)$$

in agreement with equation (6.2).

Several important results may be drawn from equations (6.20)–(6.23). First, projecting equations (6.20) and (6.21) onto $\psi_{k''}^{(\pm)}(\mathbf{r})$, exploiting equation (6.23) and replacing then k'' with k' , we obtain

$$\varepsilon_{k'k}^{(\pm)} = \varepsilon_{kk'}^{(\pm)*}, \quad (6.24)$$

i.e., the matrices of the Lagrange multipliers are Hermitian. Second, it is not difficult to verify that the DHF equations (6.20) and the boundary conditions (6.22) are invariant with respect to unitary transformations among the orbitals $\{\psi_k^{(\pm)}(\mathbf{r})\}$, in particular with respect to these transformations which diagonalize the Hermitian matrices of $\{\varepsilon_{k'k}^{(\pm)}\}$. Therefore, it is always possible, and desirable, to transform the DHF equations (6.20) to the simpler forms

$$[\hat{F}^{(\pm)} - \varepsilon_k^{(\pm)}]\psi_k^{(\pm)}(\mathbf{r}) = 0 \quad (\mathbf{r} \in \mathcal{V}), \quad (6.25)$$

with $\{\varepsilon_k^{(\pm)}\}$ real. Third, seemingly the DHF equations (6.25) and the boundary conditions (6.22) constitute two eigensystems: one for $\{\psi_k^{(+)}, \varepsilon_k^{(+)}\}$ and the second for $\{\psi_k^{(-)}, \varepsilon_k^{(-)}\}$. However, acting on equation (6.22) from the left with the operator $\gamma^{(\mp)}b^{\mp 1}i\alpha_{\perp}^{(\mp)}(\rho)$ and making use of equation (3.9) as well as of the properties

$$\alpha_{\perp}^{(\mp)}(\rho)\alpha_{\perp}^{(\pm)}(\rho) = \beta^{(\mp)}, \quad \alpha_{\perp}^{(\mp)}(\rho)\beta^{(\pm)} = \alpha_{\perp}^{(\mp)}(\rho), \quad (6.26)$$

we obtain

$$[i\alpha_{\perp}^{(\mp)}(\rho) - \gamma^{(\mp)}b^{\mp 1}\beta^{(\mp)}]\psi_k^{(\pm)}(\rho) = 0 \quad (\rho \in \mathcal{S}). \quad (6.27)$$

A glance at equation (6.25) and comparison of equations (6.22) and (6.27) show that the eigensystems obeyed by $\{\psi_k^{(+)}, \varepsilon_k^{(+)}\}$ and $\{\psi_k^{(-)}, \varepsilon_k^{(-)}\}$ are identical, so that these two sets must be the same. Consequently, the superscripts at $\{\psi_k^{(\pm)}\}$ and $\{\varepsilon_k^{(\pm)}\}$ are redundant and may be omitted. (Observe that this was by no means obvious at the beginning of this section!)

Recapitulating, we have shown that in the DHF approach the orthonormal spin orbitals $\{\psi_k(\mathbf{r})\}$, defining the best determinantal approximation $\Psi_{\text{DHF}}(\mathbf{r})$ to the eigenfunction $\Psi(\mathbf{r})$ of the system (3.1) and (3.8), are solutions to the finite-volume DHF integro-differential system

$$\hat{H}\psi_k(\mathbf{r}) + \sum_{k'=1}^N \langle \psi_{k'} | U [1 - \hat{P}_{kk'}] \psi_{k'} \rangle \psi_k(\mathbf{r}) - \varepsilon_k \psi_k(\mathbf{r}) = 0 \quad (\mathbf{r} \in \mathcal{V}) \quad (6.28)$$

augmented by the boundary conditions

$$[i\alpha_{\perp}^{(\pm)}(\rho) - \gamma^{(\pm)}b^{\pm 1}\beta^{(\pm)}]\psi_k(\rho) = 0 \quad (\rho \in \mathcal{S}) \quad (6.29)$$

(the superscripts may be chosen arbitrarily).

It remains to evaluate the DHF total energies

$$E_{\text{DHF}}^{(\pm)} = \mathcal{F}_{\text{DHF}}^{(\pm)}[\{\psi_k\}, \{\varepsilon_k\}]. \quad (6.30)$$

In virtue of equation (6.11), we have

$$\begin{aligned} E_{\text{DHF}}^{(\pm)} &= \sum_{k=1}^N \langle \psi_k | \hat{H} \psi_k \rangle + c\hbar \sum_{k=1}^N (\psi_k | [i\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)}b^{\pm 1}\beta^{(\pm)}] \psi_k) \\ &\quad + \frac{1}{2} \sum_{k,k'=1}^N \langle \langle \psi_k \psi_{k'} | U [1 - \hat{P}_{kk'}] \psi_k \psi_{k'} \rangle \rangle. \end{aligned} \quad (6.31)$$

Invoking the boundary condition (6.29), we see that the surface terms do not contribute to $E_{\text{DHF}}^{(\pm)}$. This implies that

$$E_{\text{DHF}}^{(+)} = E_{\text{DHF}}^{(-)} = E_{\text{DHF}}, \quad (6.32)$$

where, as follows from equations (6.31) and (6.28),

$$E_{\text{DHF}} = \sum_{k=1}^N \varepsilon_k - \frac{1}{2} \sum_{k,k'=1}^N \langle \langle \psi_k \psi_{k'} | U [1 - \hat{P}_{kk'}] \psi_k \psi_{k'} \rangle \rangle. \quad (6.33)$$

Evidently, estimate (6.33) is real.

7. Dependence of the DHF total energy E_{DHF} on b

In section 4 we have shown that energy eigenvalues of the spectral problem (3.1) and (3.8) are non-increasing functions of the impedance parameter b . It is remarkable that the DHF energy estimates E_{DHF} depend on b in the same manner.

To prove this fact, we differentiate equation (6.33) with respect to $b^{\pm 1}$, obtaining

$$\begin{aligned} \frac{\partial E_{\text{DHF}}}{\partial b^{\pm 1}} &= \sum_{k=1}^N \frac{\partial \varepsilon_k}{\partial b^{\pm 1}} - \sum_{k,k'=1}^N \left\langle \left\langle \frac{\partial \psi_k}{\partial b^{\pm 1}} \psi_{k'} \left| U[1 - \hat{P}_{kk'}] \psi_k \psi_{k'} \right. \right\rangle \right\rangle \\ &\quad - \sum_{k,k'=1}^N \left\langle \left\langle \psi_k \psi_{k'} \left| U[1 - \hat{P}_{kk'}] \frac{\partial \psi_k}{\partial b^{\pm 1}} \psi_{k'} \right. \right\rangle \right\rangle. \end{aligned} \tag{7.1}$$

On the other hand, differentiating the DHF equations (6.28) with respect to $b^{\pm 1}$, projecting the result onto $\psi_k(\mathbf{r})$, and summing over k , we find

$$\begin{aligned} \sum_{k=1}^N \left\langle \psi_k \left| \hat{H} \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle + \sum_{k,k'=1}^N \left\langle \left\langle \frac{\partial \psi_k}{\partial b^{\pm 1}} \psi_{k'} \left| U[1 - \hat{P}_{kk'}] \psi_k \psi_{k'} \right. \right\rangle \right\rangle \\ + 2 \sum_{k,k'=1}^N \left\langle \left\langle \psi_k \psi_{k'} \left| U[1 - \hat{P}_{kk'}] \frac{\partial \psi_k}{\partial b^{\pm 1}} \psi_{k'} \right. \right\rangle \right\rangle \\ - \sum_{k=1}^N \frac{\partial \varepsilon_k}{\partial b^{\pm 1}} - \sum_{k=1}^N \varepsilon_k \left\langle \psi_k \left| \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle = 0. \end{aligned} \tag{7.2}$$

Further, application of the three-dimensional Gauss integration theorem gives

$$\left\langle \psi_k \left| \hat{H} \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle = \left\langle \hat{H} \psi_k \left| \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle - c\hbar \left\langle \psi_k \left| i\alpha_{\perp} \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle. \tag{7.3}$$

Inserting this into equation (7.2) and exploiting the DHF equations (6.28), after some rearrangement we arrive at

$$\begin{aligned} \sum_{k=1}^N \frac{\partial \varepsilon_k}{\partial b^{\pm 1}} - \sum_{k,k'=1}^N \left\langle \left\langle \frac{\partial \psi_k}{\partial b^{\pm 1}} \psi_{k'} \left| U[1 - \hat{P}_{kk'}] \psi_k \psi_{k'} \right. \right\rangle \right\rangle \\ - \sum_{k,k'=1}^N \left\langle \left\langle \psi_k \psi_{k'} \left| U[1 - \hat{P}_{kk'}] \frac{\partial \psi_k}{\partial b^{\pm 1}} \psi_{k'} \right. \right\rangle \right\rangle = -c\hbar \sum_{k=1}^N \left\langle \psi_k \left| i\alpha_{\perp} \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle. \end{aligned} \tag{7.4}$$

Combining equations (7.1) and (7.4) leads to

$$\frac{\partial E_{\text{DHF}}}{\partial b^{\pm 1}} = -c\hbar \sum_{k=1}^N \left\langle \psi_k \left| i\alpha_{\perp} \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle. \tag{7.5}$$

The right-hand side of equation (7.5) may be further transformed with the aid of equation (6.17) and the first relation in equation (6.13). This yields

$$\frac{\partial E_{\text{DHF}}}{\partial b^{\pm 1}} = -c\hbar \sum_{k=1}^N \left\langle \psi_k \left| i\alpha_{\perp}^{(\pm)} \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle + c\hbar \sum_{k=1}^N \left\langle i\alpha_{\perp}^{(\pm)} \psi_k \left| \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle. \tag{7.6}$$

Next, exploiting the boundary condition (6.29) in the second sum on the right-hand side of equation (7.6) and utilizing the Hermiticity of $\beta^{(\pm)}$, we find

$$\frac{\partial E_{\text{DHF}}}{\partial b^{\pm 1}} = -c\hbar \sum_{k=1}^N \left\langle \psi_k \left| [i\alpha_{\perp}^{(\pm)} - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \frac{\partial \psi_k}{\partial b^{\pm 1}} \right. \right\rangle. \tag{7.7}$$

In the last step, we make use of the relationship

$$[i\alpha_{\perp}^{(\pm)}(\rho) - \gamma^{(\pm)} b^{\pm 1} \beta^{(\pm)}] \frac{\partial \psi_k(\rho)}{\partial b^{\pm 1}} = \gamma^{(\pm)} \beta^{(\pm)} \psi_k(\rho) \quad (\rho \in S), \quad (7.8)$$

resulting from differentiating the boundary condition (6.29) with respect to $b^{\pm 1}$. This gives

$$\frac{\partial E_{\text{DHF}}}{\partial b^{\pm 1}} = -c\hbar \gamma^{(\pm)} \sum_{k=1}^N (\psi_k | \beta^{(\pm)} \psi_k) \quad (7.9)$$

(cf equation (4.12)). Since $\gamma^{(+)}$ is positive and the matrix elements $\{(\psi_k | \beta^{(+)} \psi_k)\}$ are non-negative, from equation (7.9) we infer that

$$\frac{\partial E_{\text{DHF}}}{\partial b} \leq 0 \quad (7.10)$$

(cf equation (4.13)). This completes the proof of the statement made at the beginning of this section.

8. Conclusions

In this paper, we have considered stationary states of a relativistic N -electron system confined to an interior of the three-dimensional volume \mathcal{V} . The confinement has been modelled mathematically by imposing on solutions to the N -electron Dirac equation (3.1) the local impedance boundary condition (3.8) at the hypersurface enclosing the hypervolume \mathcal{V}^N . We have proved that energy eigenvalues of the resulting spectral problem are non-increasing functions of the impedance parameter appearing in the boundary condition. Next, we have discussed the possibility of exploiting the determinantal Slater functions (6.1) in the variational search for estimates of energy eigenvalues of the spectral problem (3.1) and (3.8). The functions (6.1), built of orthonormal one-electron spin orbitals, have been used in two variational principles (6.4), (6.5), obtained after modifying suitably the basic variational principles (5.31), (5.32) for energy eigenvalues of the confined system. In both cases, this resulted in the same *finite-volume* DHF eigensystem, constituted by the integro-differential equations (6.28) and the impedance boundary conditions (6.29), satisfied by the optimal spin orbitals. Finally, we have proved that the DHF estimates (6.33) of the exact energy eigenvalues retain the property of the latter of being non-increasing functions of the impedance parameter.

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Appendix A. Some properties of the operators $\hat{\mathcal{A}}_{\perp}^{(\pm)}$ and $\hat{\mathcal{B}}^{(\pm)}$

It may be inferred from definitions (3.10)–(3.14) and from the well-known properties of the Dirac matrices α and β [7] that the operators $\hat{\mathcal{A}}_{\perp}^{(\pm)}$ and $\hat{\mathcal{B}}^{(\pm)}$ obey

$$\hat{\mathcal{A}}_{\perp}^{(+)} + \hat{\mathcal{A}}_{\perp}^{(-)} = \hat{\mathcal{A}}_{\perp}, \quad (A.1)$$

$$\hat{\mathcal{B}}^{(\pm)} \hat{\mathcal{B}}^{(\pm)} = \hat{\mathcal{B}}^{(\pm)}, \quad \hat{\mathcal{B}}^{(\pm)} \hat{\mathcal{B}}^{(\mp)} = 0, \quad (A.2)$$

$$\hat{\mathcal{A}}_{\perp}^{(\pm)} \hat{\mathcal{A}}_{\perp}^{(\pm)} = 0, \quad \hat{\mathcal{A}}_{\perp}^{(\pm)} \hat{\mathcal{A}}_{\perp}^{(\mp)} = \hat{\mathcal{B}}^{(\pm)}, \quad (A.3)$$

$$\hat{\mathcal{A}}_{\perp}^{(\pm)} \hat{\mathcal{B}}^{(\pm)} = 0, \quad \hat{\mathcal{A}}_{\perp}^{(\pm)} \hat{\mathcal{B}}^{(\mp)} = \hat{\mathcal{A}}_{\perp}^{(\pm)}, \quad (A.4)$$

$$\hat{\mathcal{B}}^{(\pm)} \hat{\mathcal{A}}_{\perp}^{(\pm)} = \hat{\mathcal{A}}_{\perp}^{(\pm)}, \quad \hat{\mathcal{B}}^{(\pm)} \hat{\mathcal{A}}_{\perp}^{(\mp)} = 0. \quad (A.5)$$

Moreover, for any two sufficiently regular 4^N -component spinor functions $\Phi(\varrho)$ and $\Phi'(\varrho)$ it holds

$$(\Phi|\hat{A}_\perp^{(\pm)}\Phi')_{\mathfrak{S}} = (\hat{A}_\perp^{(\mp)}\Phi|\Phi')_{\mathfrak{S}}, \quad (\Phi|\hat{\beta}^{(\pm)}\Phi')_{\mathfrak{S}} = (\hat{\beta}^{(\pm)}\Phi|\Phi')_{\mathfrak{S}}. \quad (\text{A.6})$$

Appendix B. Equivalence of boundary conditions in equation (3.8)

Consider the boundary condition corresponding to the choice of the upper superscripts in equation (3.8):

$$[i\hat{A}_\perp^{(+)} - \gamma^{(+)}b\hat{\beta}^{(+)}]\Psi(\varrho) = 0 \quad (\varrho \in \mathfrak{S}). \quad (\text{B.1})$$

Operating on equation (A.1) from the left with $-\gamma^{(-)}b^{-1}i\hat{A}_\perp^{(-)}$ and making use of equations (3.9), (A.3) and (A.4), transforms equation (B.1) into

$$[i\hat{A}_\perp^{(-)} - \gamma^{(-)}b^{-1}\hat{\beta}^{(-)}]\Psi(\varrho) = 0 \quad (\varrho \in \mathfrak{S}). \quad (\text{B.2})$$

Hence, it follows that superscripts in equation (3.8) may be chosen arbitrarily.

Appendix C. Derivation of equation (6.9)

Consider the matrix element $(\overline{\Psi}_{\text{DHF}}^{(\pm)}|\hat{\beta}^{(\pm)}\overline{\Psi}_{\text{DHF}}^{(\pm)})_{\mathfrak{S}}$. Since

$$\begin{aligned} \overline{\Psi}_{\text{DHF}}^{(\pm)}(\varrho_K) &= \frac{1}{\sqrt{N!}} \sum_{k_1=1}^N \cdots \sum_{k_N=1}^N \epsilon_{k_1 \dots k_N} \overline{\psi}_{k_1}^{(\pm)}(\mathbf{r}_1) \otimes \cdots \otimes \overline{\psi}_{k_{K-1}}^{(\pm)}(\mathbf{r}_{K-1}) \otimes \overline{\psi}_{k_K}^{(\pm)}(\rho_K) \\ &\quad \otimes \overline{\psi}_{k_{K+1}}^{(\pm)}(\mathbf{r}_{K+1}) \otimes \cdots \otimes \overline{\psi}_{k_N}^{(\pm)}(\mathbf{r}_N) \quad (\varrho_K \in \mathfrak{S}_K), \end{aligned} \quad (\text{C.1})$$

after employing equations (3.10) and (3.11), we have

$$\begin{aligned} (\overline{\Psi}_{\text{DHF}}^{(\pm)}|\hat{\beta}^{(\pm)}\overline{\Psi}_{\text{DHF}}^{(\pm)})_{\mathfrak{S}} &= \frac{1}{N!} \sum_{K=1}^N \sum_{k_1=1}^N \cdots \sum_{k_N=1}^N \sum_{k'_1=1}^N \cdots \sum_{k'_N=1}^N \epsilon_{k_1 \dots k_N} \epsilon_{k'_1 \dots k'_N} \\ &\quad \times \langle \overline{\psi}_{k_1}^{(\pm)} | \overline{\psi}_{k'_1}^{(\pm)} \rangle \cdots \langle \overline{\psi}_{k_{K-1}}^{(\pm)} | \overline{\psi}_{k'_{K-1}}^{(\pm)} \rangle \langle \overline{\psi}_{k_K}^{(\pm)} | \beta^{(\pm)} \overline{\psi}_{k'_K}^{(\pm)} \rangle \\ &\quad \times \langle \overline{\psi}_{k_{K+1}}^{(\pm)} | \overline{\psi}_{k'_{K+1}}^{(\pm)} \rangle \cdots \langle \overline{\psi}_{k_N}^{(\pm)} | \overline{\psi}_{k'_N}^{(\pm)} \rangle. \end{aligned} \quad (\text{C.2})$$

Exploiting then the orthonormality constraint (6.2), and also making use of the summation formula

$$\sum_{k_1=1}^N \cdots \sum_{k_{K-1}=1}^N \sum_{k_{K+1}=1}^N \cdots \sum_{k_N=1}^N \epsilon_{k_1 \dots k_{K-1} k_K k_{K+1} \dots k_N} \epsilon_{k_1 \dots k_{K-1} k'_K k_{K+1} \dots k_N} = (N-1)! \delta_{k_K k'_K}, \quad (\text{C.3})$$

we arrive at

$$(\overline{\Psi}_{\text{DHF}}^{(\pm)}|\hat{\beta}^{(\pm)}\overline{\Psi}_{\text{DHF}}^{(\pm)})_{\mathfrak{S}} = \frac{1}{N} \sum_{K=1}^N \sum_{k_K=1}^N (\overline{\psi}_{k_K}^{(\pm)} | \beta^{(\pm)} \overline{\psi}_{k_K}^{(\pm)}), \quad (\text{C.4})$$

hence, it follows immediately that

$$(\overline{\Psi}_{\text{DHF}}^{(\pm)}|\hat{\beta}^{(\pm)}\overline{\Psi}_{\text{DHF}}^{(\pm)})_{\mathfrak{S}} = \sum_{k=1}^N (\overline{\psi}_k^{(\pm)} | \beta^{(\pm)} \overline{\psi}_k^{(\pm)}). \quad (\text{C.5})$$

In the completely analogous way one shows that

$$(\overline{\Psi}_{\text{DHF}}^{(\pm)}|i\hat{A}_\perp^{(\pm)}\overline{\Psi}_{\text{DHF}}^{(\pm)})_{\mathfrak{S}} = \sum_{k=1}^N (\overline{\psi}_k^{(\pm)} | i\alpha_\perp^{(\pm)} \overline{\psi}_k^{(\pm)}). \quad (\text{C.6})$$

Equation (6.9) results from equations (C.6) and (C.5).

References

- [1] Jaskólski W 1996 *Phys. Rep.* **271** 1
- [2] Connerade J P and Semaoune R 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 869
- [3] Connerade J P and Semaoune R 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** 3467
- [4] Connerade J P, Kengkan P, Lakshmi P A and Semaoune R 2000 *J. Phys. B: At. Mol. Opt. Phys.* **33** L847
- [5] Connerade J P, Kengkan P and Semaoune R 2001 *J. Chin. Chem. Soc. (Taipei)* **48** 265
- [6] Gerjuoy E, Rau A R P and Spruch L 1983 *Rev. Mod. Phys.* **55** 725
- [7] Schiff L I 1968 *Quantum Mechanics* 3rd edn (New York: McGraw-Hill)