
Variational Principles for Bound States of Schrödinger and Dirac Equations Allowing the Use of Discontinuous Trial Functions

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ABSTRACT: We present systematic constructions of variational principles for energies of bound states of the Schrödinger and Dirac equations. The principles allow the use of discontinuous trial functions. The method employed is based on a generalized Lagrange procedure. Relationships between our variational principles and those available in the literature are established. © 2004 Wiley Periodicals, Inc. *Int J Quantum Chem* 97: 966–976, 2004

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1. Introduction

Among various methods used for approximate solving of the quantum mechanical energy eigenproblem, written here compactly as

$$[\hat{H} - E]\Psi(\mathbf{r}) = 0, \quad (1.1)$$

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a variational method, based on the Rayleigh principle

$$\delta F[\Psi] = 0, \quad E = F[\Psi], \quad (1.2)$$

with the functional

$$F[\bar{\Psi}] = \frac{\langle \bar{\Psi} | \hat{H} \bar{\Psi} \rangle}{\langle \bar{\Psi} | \bar{\Psi} \rangle}, \quad (1.3)$$

belongs to the most efficient. In the case of a single unconfined particle, which will be studied in this work, the scalar product in Eq. (1.3) is defined as

$$\langle \Phi | \Phi' \rangle = \int_{\mathbb{R}^3} d^3\mathbf{r} \Phi^*(\mathbf{r}) \Phi'(\mathbf{r}), \quad (1.4)$$

where $d^3\mathbf{r}$ is an infinitesimal volume element around the point \mathbf{r} , while the symbol $*$ denotes the complex conjugation if \hat{H} is the Schrödinger Hamiltonian or the Hermitian conjugation if \hat{H} is the Dirac Hamiltonian.

In applying the principle (1.2)–(1.3), it is crucial to ensure that the trial function $\Psi(\mathbf{r})$ satisfies some regularity conditions. First, $\Psi(\mathbf{r})$ should be single valued. Second, if a differential rather than integral form of the Hamiltonian is known, which is nearly always the case, some continuity restrictions have to be imposed on $\Psi(\mathbf{r})$: if \hat{H} is the Dirac Hamiltonian, the function $\Psi(\mathbf{r})$ should be continuous in all its components; if \hat{H} is the Schrödinger Hamiltonian, both the function $\Psi(\mathbf{r})$ and its gradient $\nabla\Psi(\mathbf{r})$ should be continuous.

In some quantum problems, primarily in molecular and solid-state physics, a relevant configuration space may be divided in a natural way into disjoint regions where an exact eigenfunction is expected to have substantially different behaviors (e.g., being monotonic in one region and highly oscillatory in another). It has been pointed out by a number of investigators [1–18] that in solving such problems it might be advantageous to work with trial functions having discontinuities at interfaces.

Discontinuous trial functions cannot be used in the principle (1.2)–(1.3). This does not mean, however, that they are illegitimate from the standpoint of the variational method. To use such functions, one has to replace the simple functional (1.3) by a more general one, differing from (1.3) in the way in which the continuity requirements imposed on exact eigenfunctions are built in it. Several versions of this more general functional may be found in the literature [1–6, 10–18]; among them, that proposed in Ref. [4] was devised for the Dirac particle, while others are suitable for the Schrödinger Hamiltonian.

The variational principles from Refs. [1–6, 10–18] have been obtained by using a wide range of specific approaches; some have simply been guessed. In those circumstances, there is a need for a systematic derivation of general variational principles, which allow the use of discontinuous trial functions. This is the purpose of the present study. We shall employ a powerful (but, regrettably, still not appreciated enough) procedure that is a generalization of the method of Lagrange multipliers

[19]. For the sake of brevity, we restrict our considerations to a single unconfined particle with its configuration space divided into two domains. Generalizations to many-particle systems or to a larger number of domains are straightforward. The case of the Schrödinger equation is studied in section 2, while that of the Dirac equation in section 3.

In this work, we focus on theory. Numerical illustrations, for both the Schrödinger and Dirac equations, will be presented in forthcoming papers.

2. Schrödinger Equation

2.1. CONSTRUCTION OF A FUNDAMENTAL FUNCTIONAL

Let us assume that the local, real potential in the Schrödinger Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad (2.1)$$

is such that it is convenient to divide the whole configuration space \mathbb{R}^3 into two regions: a finite region V_1 and the infinite remainder $V_2 = \mathbb{R}^3 \setminus V_1$, joined over a (sufficiently smooth) surface \mathcal{S} (Fig. 1). A position vector of a point in V_1 or V_2 will be denoted by \mathbf{r} ; for a point lying on the interface \mathcal{S} , we shall use the symbol $\boldsymbol{\rho}$ instead of \mathbf{r} . A unit vector normal to the surface \mathcal{S} at the point $\boldsymbol{\rho}$, with sense from V_1 to V_2 , will be denoted by $\mathbf{n}(\boldsymbol{\rho})$. Adopting the notation

$$\Psi_i(\mathbf{r}) = \Psi(\mathbf{r}) \quad (\mathbf{r} \in V_i), \quad (2.2)$$

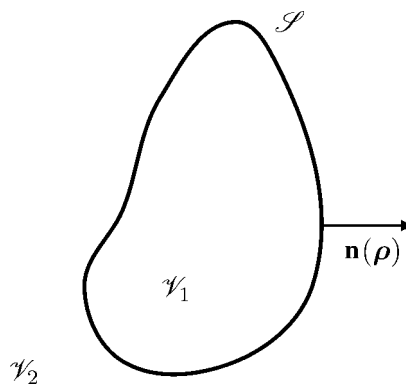


FIGURE 1. Partitioning of \mathbb{R}^3 into the finite domain V_1 and the infinite remainder V_2 , separated by the surface \mathcal{S} ; $\mathbf{n}(\boldsymbol{\rho})$ is the unit vector normal to the surface \mathcal{S} at the point $\boldsymbol{\rho}$.

the energy eigenproblem (1.1) may be rewritten as

$$[\hat{H} - E]\Psi_1(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_1), \quad (2.3)$$

$$[\hat{H} - E]\Psi_2(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_2), \quad (2.4)$$

with the usual requirements of single-valuedness and finiteness, with the asymptotic condition

$$r\Psi_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0, \quad (2.5)$$

and with the following subsidiary continuity conditions imposed at the interface \mathcal{S} :

$$\Psi_1(\boldsymbol{\rho}) - \Psi_2(\boldsymbol{\rho}) = 0, \quad (2.6)$$

$$\nabla_{\perp}\Psi_1(\boldsymbol{\rho}) - \nabla_{\perp}\Psi_2(\boldsymbol{\rho}) = 0, \quad (2.7)$$

where

$$\nabla_{\perp}\Psi_i(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho}) \cdot \nabla\Psi_i(\mathbf{r})|_{\mathbf{r}=\boldsymbol{\rho}} \quad (2.8)$$

is the normal derivative of $\Psi_i(\mathbf{r})$ at the surface point $\boldsymbol{\rho}$.

Following the prescription of Gerjuoy et al. [19], we start with the following provisional form of the sought energy functional:

$$\begin{aligned} F[\bar{E}, \bar{\Psi}_1, \bar{\Psi}_2; \bar{\Lambda}_1, \bar{\Lambda}_2, \bar{\lambda}, \bar{\chi}] &= \bar{E} + \langle \bar{\Lambda}_1 | [\hat{H} - \bar{E}] \bar{\Psi}_1 \rangle_1 \\ &+ \langle \bar{\Lambda}_2 | [\hat{H} - \bar{E}] \bar{\Psi}_2 \rangle_2 + \langle \bar{\lambda} | \bar{\Psi}_1 - \bar{\Psi}_2 \rangle \\ &+ \langle \bar{\chi} | \nabla_{\perp} \bar{\Psi}_1 - \nabla_{\perp} \bar{\Psi}_2 \rangle. \end{aligned} \quad (2.9)$$

The volume and surface scalar products appearing in Eq. (2.9) are defined as

$$\langle \Phi | \Phi' \rangle_i = \int_{V_i} d^3\mathbf{r} \Phi^*(\mathbf{r}) \Phi'(\mathbf{r}), \quad (2.10)$$

(the surface \mathcal{S} is excluded from the integration domain) and

$$\langle \Phi | \Phi' \rangle = \int_{\mathcal{S}} d^2\boldsymbol{\rho} \Phi^*(\boldsymbol{\rho}) \Phi'(\boldsymbol{\rho}) \quad (2.11)$$

(here $d^2\boldsymbol{\rho}$ is an infinitesimal scalar surface element of \mathcal{S} around the point $\boldsymbol{\rho}$), respectively, where $*$ denotes the complex conjugation. Quantities \bar{E} , $\bar{\Psi}_1(\mathbf{r})$, and $\bar{\Psi}_2(\mathbf{r})$, with the latter obeying

$$r\bar{\Psi}_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0, \quad (2.12)$$

are some trial estimates of E , $\Psi_1(\mathbf{r})$, and $\Psi_2(\mathbf{r})$, respectively, while $\bar{\Lambda}_1(\mathbf{r})$ (with $\mathbf{r} \in V_1$), $\bar{\Lambda}_2(\mathbf{r})$ (with $\mathbf{r} \in V_2$), $\bar{\lambda}(\boldsymbol{\rho})$, and $\bar{\chi}(\boldsymbol{\rho})$ are Lagrange functions incorporating Eqs. (2.3), (2.4), (2.6), and (2.7), respectively, as constraints. To make the integral over V_2 convergent, in addition to Eq. (2.12) we impose

$$r\bar{\Lambda}_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0. \quad (2.13)$$

Evidently, the functional (2.9) possesses the desired property

$$F[E, \Psi_1, \Psi_2; \bar{\Lambda}_1, \bar{\Lambda}_2, \bar{\lambda}, \bar{\chi}] = E. \quad (2.14)$$

The first variation of the functional (2.9) due to arbitrary variations in \bar{E} , $\bar{\Psi}_1(\mathbf{r})$, $\bar{\Psi}_2(\mathbf{r})$ about E , $\Psi_1(\mathbf{r})$, $\Psi_2(\mathbf{r})$ and in $\bar{\Lambda}_1(\mathbf{r})$, $\bar{\Lambda}_2(\mathbf{r})$, $\bar{\lambda}(\boldsymbol{\rho})$, $\bar{\chi}(\boldsymbol{\rho})$ about $\Lambda_1(\mathbf{r})$, $\Lambda_2(\mathbf{r})$, $\lambda(\boldsymbol{\rho})$, $\chi(\boldsymbol{\rho})$ (with the latter four functions chosen at this stage arbitrarily) is

$$\begin{aligned} \delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda, \chi] &= \delta E + \langle \delta\Lambda_1 | [\hat{H} - E] \Psi_1 \rangle_1 - \delta E \langle \Lambda_1 | \Psi_1 \rangle_1 \\ &+ \langle \Lambda_1 | [\hat{H} - E] \delta\Psi_1 \rangle_1 + \langle \delta\Lambda_2 | [\hat{H} - E] \Psi_2 \rangle_2 \\ &- \delta E \langle \Lambda_2 | \Psi_2 \rangle_2 + \langle \Lambda_2 | [\hat{H} - E] \delta\Psi_2 \rangle_2 + (\delta\lambda | \Psi_1 - \Psi_2) \\ &+ (\lambda | \delta\Psi_1 - \delta\Psi_2) + (\delta\chi | \nabla_{\perp} \Psi_1 - \nabla_{\perp} \Psi_2) \\ &+ (\chi | \nabla_{\perp} \delta\Psi_1 - \nabla_{\perp} \delta\Psi_2). \end{aligned} \quad (2.15)$$

We emphasize that the variations δE , $\delta\Psi_1$, and $\delta\Psi_2$ need not conform to the constraints (2.3), (2.4), (2.6), and (2.7); the only requirements we impose are that the variations be sufficiently smooth in interiors of the domains V_i and that

$$r\delta\Psi_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0, \quad (2.16)$$

which is the direct consequence of Eqs. (2.5) and (2.12). Equation (2.15) may be simplified considerably. Indeed, Eqs. (2.3), (2.4), (2.6), and (2.7) imply that the second, fifth, eighth, and tenth terms on the right-hand side of Eq. (2.15) vanish, hence, we obtain

$$\begin{aligned} \delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda, \chi] = & \delta E[1 - \langle \Lambda_1 | \Psi_1 \rangle_1 \\ & - \langle \Lambda_2 | \Psi_2 \rangle_2] + \langle \Lambda_1 | [\hat{H} - E] \delta \Psi_1 \rangle_1 \\ & + \langle \Lambda_2 | [\hat{H} - E] \delta \Psi_2 \rangle_2 + (\lambda | \delta \Psi_1 - \delta \Psi_2 \rangle \\ & + (\chi | \nabla_{\perp} \delta \Psi_1 - \nabla_{\perp} \delta \Psi_2 \rangle. \quad (2.17) \end{aligned}$$

From the Green integration theorem and the reality of E , we have

$$\begin{aligned} \langle \Lambda_1 | [\hat{H} - E] \delta \Psi_1 \rangle_1 = & \langle [\hat{H} - E] \Lambda_1 | \delta \Psi_1 \rangle_1 \\ & + \frac{\hbar^2}{2m} (\nabla_{\perp} \Lambda_1 | \delta \Psi_1 \rangle - \frac{\hbar^2}{2m} (\Lambda_1 | \nabla_{\perp} \delta \Psi_1 \rangle, \quad (2.18) \end{aligned}$$

$$\begin{aligned} \langle \Lambda_2 | [\hat{H} - E] \delta \Psi_2 \rangle_2 = & \langle [\hat{H} - E] \Lambda_2 | \delta \Psi_2 \rangle_2 \\ & - \frac{\hbar^2}{2m} (\nabla_{\perp} \Lambda_2 | \delta \Psi_2 \rangle + \frac{\hbar^2}{2m} (\Lambda_2 | \nabla_{\perp} \delta \Psi_2 \rangle. \quad (2.19) \end{aligned}$$

In Eq. (2.19), surface integrals over the sphere at infinity have been omitted by virtue of Eq. (2.16) and the fact that $\Lambda_2(\mathbf{r})$, as a particular case of $\Lambda_2(\mathbf{r})$, obeys the condition (2.13). Employing Eqs. (2.18) and (2.19), we arrive at the following final form of the first variation of the functional (2.9):

$$\begin{aligned} \delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda, \chi] = & \delta E[1 - \langle \Lambda_1 | \Psi_1 \rangle_1 \\ & - \langle \Lambda_2 | \Psi_2 \rangle_2] + \langle [\hat{H} - E] \Lambda_1 | \delta \Psi_1 \rangle_1 \\ & + \langle [\hat{H} - E] \Lambda_2 | \delta \Psi_2 \rangle_2 + \left(\lambda + \frac{\hbar^2}{2m} \nabla_{\perp} \Lambda_1 \middle| \delta \Psi_1 \right) \\ & - \left(\lambda + \frac{\hbar^2}{2m} \nabla_{\perp} \Lambda_2 \middle| \delta \Psi_2 \right) + \left(\chi - \frac{\hbar^2}{2m} \Lambda_1 \middle| \nabla_{\perp} \delta \Psi_1 \right) \\ & - \left(\chi - \frac{\hbar^2}{2m} \Lambda_2 \middle| \nabla_{\perp} \delta \Psi_2 \right). \quad (2.20) \end{aligned}$$

So far, the Lagrange functions $\Lambda_1(\mathbf{r})$, $\Lambda_2(\mathbf{r})$, $\lambda(\boldsymbol{\rho})$, and $\chi(\boldsymbol{\rho})$ have been arbitrary apart from the constraint (2.13) imposed on $\Lambda_2(\mathbf{r})$. At this moment, however, we demand that they are such that the first variation of the functional (2.9) vanishes for arbitrary [cf. however, Eq. (2.16)] variations appearing in Eq. (2.20), i.e.,

$$\delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda, \chi] = 0. \quad (2.21)$$

Evidently, this occurs if and only if the functions $\Lambda_1(\mathbf{r})$, $\Lambda_2(\mathbf{r})$, $\lambda(\boldsymbol{\rho})$, and $\chi(\boldsymbol{\rho})$ obey

$$1 - \langle \Lambda_1 | \Psi_1 \rangle_1 - \langle \Lambda_2 | \Psi_2 \rangle_2 = 0, \quad (2.22)$$

$$[\hat{H} - E] \Lambda_1(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_1), \quad (2.23)$$

$$[\hat{H} - E] \Lambda_2(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_2), \quad (2.24)$$

$$\lambda(\boldsymbol{\rho}) + \frac{\hbar^2}{2m} \nabla_{\perp} \Lambda_1(\boldsymbol{\rho}) = 0, \quad (2.25)$$

$$\lambda(\boldsymbol{\rho}) + \frac{\hbar^2}{2m} \nabla_{\perp} \Lambda_2(\boldsymbol{\rho}) = 0, \quad (2.26)$$

$$\chi(\boldsymbol{\rho}) - \frac{\hbar^2}{2m} \Lambda_1(\boldsymbol{\rho}) = 0, \quad (2.27)$$

$$\chi(\boldsymbol{\rho}) - \frac{\hbar^2}{2m} \Lambda_2(\boldsymbol{\rho}) = 0. \quad (2.28)$$

The first conclusion we infer from the system (2.22)–(2.28) is that at the surface \mathcal{S} the functions $\Lambda_1(\mathbf{r})$ and $\Lambda_2(\mathbf{r})$ match smoothly:

$$\Lambda_1(\boldsymbol{\rho}) = \Lambda_2(\boldsymbol{\rho}), \quad (2.29)$$

$$\nabla_{\perp} \Lambda_1(\boldsymbol{\rho}) = \nabla_{\perp} \Lambda_2(\boldsymbol{\rho}). \quad (2.30)$$

Next, on comparing Eqs. (2.23), (2.24), (2.29), (2.30), and (2.13) with Eqs. (2.3), (2.4), (2.6), (2.7), and (2.5), we see that $\Lambda_1(\mathbf{r})$ and $\Lambda_2(\mathbf{r})$ obey the same homogeneous differential equations and the same matching conditions as the functions $\Psi_1(\mathbf{r})$ and $\Psi_2(\mathbf{r})$. This allows us to choose

$$\Lambda_1(\mathbf{r}) = \eta \Psi_1(\mathbf{r}), \quad (2.31)$$

$$\Lambda_2(\mathbf{r}) = \eta \Psi_2(\mathbf{r}), \quad (2.32)$$

where η is some constant to be determined. This may be done with the aid of Eq. (2.22). Indeed, substituting Eqs. (2.31) and (2.32) into this equation, we find that η is real and given by

$$\eta = \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2}. \quad (2.33)$$

Hence, we have

$$\Lambda_1(\mathbf{r}) = \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} \Psi_1(\mathbf{r}), \quad (2.34)$$

$$\Lambda_2(\mathbf{r}) = \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} \Psi_2(\mathbf{r}). \quad (2.35)$$

Further, from Eqs. (2.25)–(2.28), (2.34), and (2.35) we find

$$\lambda(\boldsymbol{\rho}) = -\frac{\hbar^2}{2m} \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} \times [a \nabla_{\perp} \Psi_1(\boldsymbol{\rho}) + (1-a) \nabla_{\perp} \Psi_2(\boldsymbol{\rho})], \quad (2.36)$$

$$\chi(\boldsymbol{\rho}) = \frac{\hbar^2}{2m} \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} \times [b \Psi_1(\boldsymbol{\rho}) + (1-b) \Psi_2(\boldsymbol{\rho})], \quad (2.37)$$

where a and b are arbitrary complex constants.

It is both natural and desirable to choose the Lagrange functions $\bar{\Lambda}_1(\mathbf{r})$, $\bar{\Lambda}_2(\mathbf{r})$, $\bar{\lambda}(\boldsymbol{\rho})$, and $\bar{\chi}(\boldsymbol{\rho})$, appearing in the functional (2.9), so that relations analogous to (2.34)–(2.37) hold between these functions and the estimates $\bar{\Psi}_1(\mathbf{r})$ and $\bar{\Psi}_2(\mathbf{r})$:

$$\bar{\Lambda}_1(\mathbf{r}) = \frac{1}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \bar{\Psi}_1(\mathbf{r}), \quad (2.38)$$

$$\bar{\Lambda}_2(\mathbf{r}) = \frac{1}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \bar{\Psi}_2(\mathbf{r}), \quad (2.39)$$

$$\bar{\lambda}(\boldsymbol{\rho}) = -\frac{\hbar^2}{2m} \frac{1}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \times [a \nabla_{\perp} \bar{\Psi}_1(\boldsymbol{\rho}) + (1-a) \nabla_{\perp} \bar{\Psi}_2(\boldsymbol{\rho})], \quad (2.40)$$

$$\bar{\chi}(\boldsymbol{\rho}) = \frac{\hbar^2}{2m} \frac{1}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \times [b \bar{\Psi}_1(\boldsymbol{\rho}) + (1-b) \bar{\Psi}_2(\boldsymbol{\rho})]. \quad (2.41)$$

On substituting Eqs. (2.38)–(2.41) into Eq. (2.9), we obtain the following form of the sought energy functional:

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - \frac{\hbar^2 (a \nabla_{\perp} \bar{\Psi}_1 + [1-a] \nabla_{\perp} \bar{\Psi}_2 | \bar{\Psi}_1 - \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 (b \bar{\Psi}_1 + [1-b] \bar{\Psi}_2 | \nabla_{\perp} \bar{\Psi}_1 - \nabla_{\perp} \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}, \quad (2.42)$$

which does not contain the energy estimate \bar{E} . It is clear from the method of its construction, and may be also easily verified by inspection, that the functional (2.42) possesses the required properties

$$E = F[\Psi_1, \Psi_2] \quad (2.43)$$

and

$$\delta F[\Psi_1, \Psi_2] = 0. \quad (2.44)$$

For reasons that will become clear in section 2.4, hereafter the functional (2.42) will be termed the fundamental functional.

2.2. CONSTRAINED TRIAL FUNCTIONS

During the course of the derivation of the fundamental functional (2.42), we have not imposed any continuity conditions on the trial functions $\bar{\Psi}_1(\mathbf{r})$ and $\bar{\Psi}_2(\mathbf{r})$ at the interface \mathcal{S} . It seems interesting to investigate how the functional (2.42) is influenced if we impose such conditions.

If the trial functions are constrained to match at \mathcal{S} :

$$\bar{\Psi}_1(\boldsymbol{\rho}) = \bar{\Psi}_2(\boldsymbol{\rho}), \quad (2.45)$$

the functional (2.42) simplifies to

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 (\bar{\Psi}_1 | \nabla_{\perp} \bar{\Psi}_1 - \nabla_{\perp} \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (2.46)$$

If instead of Eq. (2.45) the constraint

$$\nabla_{\perp} \bar{\Psi}_1(\boldsymbol{\rho}) = \nabla_{\perp} \bar{\Psi}_2(\boldsymbol{\rho}) \quad (2.47)$$

is imposed, the functional (2.42) becomes

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - \frac{\hbar^2 (\nabla_{\perp} \bar{\Psi}_1 | \bar{\Psi}_1 - \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (2.48)$$

Finally, if the constraints (2.45) and (2.47) are satisfied simultaneously, Eq. (2.42) yields the functional

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}, \quad (2.49)$$

which, in virtue of the additivity of integrals, is identical with the functional (1.3). It is worth noting that, contrary to the unconstrained functional

(2.42), none of the functionals (2.46), (2.48), and (2.49) depends on the parameters a and b .

2.3. REAL FORM OF THE FUNDAMENTAL FUNCTIONAL

Energy eigenvalues of the Hamiltonian (2.1) are known to be real and it would be desirable if their estimates yielded by the functional (2.42) possessed the same property. It appears, however, that this is not the case unless an additional constraint is imposed on the parameters a and b . To find this constraint, we note that with the aid of the Green theorem the complex conjugate of Eq. (2.42) is transformed into

$$F^*[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - \frac{\hbar^2 ([1 - b^*] \nabla_{\perp} \bar{\Psi}_1 + b^* \nabla_{\perp} \bar{\Psi}_2 | \bar{\Psi}_1)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 ([1 - b^*] \nabla_{\perp} \bar{\Psi}_1 + b^* \nabla_{\perp} \bar{\Psi}_2 | \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 ([1 - a^*] \bar{\Psi}_1 + a^* \bar{\Psi}_2 | \nabla_{\perp} \bar{\Psi}_1)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 ([1 - a^*] \bar{\Psi}_1 + a^* \bar{\Psi}_2 | \nabla_{\perp} \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (2.50)$$

Then, comparison of Eqs. (2.42) and (2.50) shows that the necessary and sufficient condition for the relationship

$$F^*[\bar{\Psi}_1, \bar{\Psi}_2] = F[\Psi_1, \Psi_2] \quad (2.51)$$

being satisfied for arbitrary trial functions is

$$b = 1 - a^*. \quad (2.52)$$

We conclude that the particular form of the functional (2.42) possessing the property of being real is

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - \frac{\hbar^2 (a \nabla_{\perp} \bar{\Psi}_1 + [1 - a] \nabla_{\perp} \bar{\Psi}_2 | \bar{\Psi}_1 - \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 ([1 - a^*] \bar{\Psi}_1 + a^* \bar{\Psi}_2 | \nabla_{\perp} \bar{\Psi}_1 - \nabla_{\perp} \bar{\Psi}_2)}{2m \langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \quad (2.53)$$

with a arbitrary complex.

2.4. GENERALIZATION OF THE FUNDAMENTAL FUNCTIONAL

The fundamental functional (2.42) is not the most general functional admitting trial functions with discontinuities at \mathcal{S} . To show this, let us consider a functional of the form

$$\mathcal{F}[\bar{\Psi}_1, \bar{\Psi}_2] = F[\bar{\Psi}_1, \bar{\Psi}_2] + \sum_n (\bar{A}^{(n)} | \bar{B}^{(n)}), \quad (2.54)$$

where

$$\bar{A}^{(n)} \equiv A^{(n)}[\bar{\Psi}_1, \bar{\Psi}_2; \rho] \quad (2.55)$$

and

$$\bar{B}^{(n)} \equiv B^{(n)}[\bar{\Psi}_1, \bar{\Psi}_2; \rho], \quad (2.56)$$

obeying

$$A^{(n)}[\Psi_1, \Psi_2; \rho] = 0, \quad (2.57)$$

$$B^{(n)}[\Psi_1, \Psi_2; \rho] = 0, \quad (2.58)$$

are otherwise arbitrary functionals of $\bar{\Psi}_i$ and functions of ρ . Because of Eqs. (2.43), (2.57), and (2.58), we have

$$E = \mathcal{F}[\Psi_1, \Psi_2]. \quad (2.59)$$

Further, since

$$\delta \mathcal{F}[\Psi_1, \Psi_2] = \delta F[\Psi_1, \Psi_2] + \sum_n (\delta A^{(n)} | B^{(n)}) + \sum_n (A^{(n)} | \delta B^{(n)}), \quad (2.60)$$

with the aid of Eqs. (2.44), (2.57), and (2.58), we infer that, in addition to (2.59), the functional (2.54) possesses the required stationarity property

$$\delta \mathcal{F}[\Psi_1, \Psi_2] = 0. \quad (2.61)$$

2.5. RELATIONSHIP TO PREVIOUS WORKS

Leigh [1] considered a linear functional equivalent to the fractional functional

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{\hbar^2 (\bar{\Psi}_2 | \nabla_\perp \bar{\Psi}_1) - (\nabla_\perp \bar{\Psi}_2 | \bar{\Psi}_1)}{2m (\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2)}, \quad (2.62)$$

while Trail and Bird [17] worked with a functional that may be obtained from (2.62) by replacing in the latter $(\nabla_\perp \bar{\Psi}_2 | \bar{\Psi}_1)$ with $(\bar{\Psi}_1 | \nabla_\perp \bar{\Psi}_2)$. Both functionals may be obtained from our fundamental functional (2.42) setting there

$$a = b = \frac{1}{2} \quad (2.63)$$

and admitting only real trial functions (this limitation was not recognized in Refs. [1 and 17]). The functional (2.62) (respectively, its linear analogue) was employed correctly, with real trial functions, by Weare and Parr [6], Stuebing et al. [14], and Brownstein [16] (respectively, McCavert and Rudge [10]). Schlosser and Marcus [3] and Brownstein and Zhou [18] suggested the use of complex trial functions in a functional defined as a real part of the functional (2.62). It is easily verifiable that their functional is a particular case of our fundamental functional (2.42) with a and b given by Eq. (2.63). Inglesfield [15] used the functional (2.46) as a starting point for formulating a nonrelativistic embedding method. Finally, Marcus [5] considered the generalized functional (2.54) with

$$A^{(1)}[\bar{\Psi}_1, \bar{\Psi}_2; \boldsymbol{\rho}] = \bar{\Psi}_1(\boldsymbol{\rho}) - \bar{\Psi}_2(\boldsymbol{\rho}), \quad (2.64)$$

$$B^{(1)}[\bar{\Psi}_1, \bar{\Psi}_2; \boldsymbol{\rho}] = \frac{c^{(1)}}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \times [\bar{\Psi}_1(\boldsymbol{\rho}) - \bar{\Psi}_2(\boldsymbol{\rho})], \quad (2.65)$$

$$A^{(2)}[\bar{\Psi}_1, \bar{\Psi}_2; \boldsymbol{\rho}] = \nabla_\perp \bar{\Psi}_1(\boldsymbol{\rho}) - \nabla_\perp \bar{\Psi}_2(\boldsymbol{\rho}), \quad (2.66)$$

and

$$B^{(2)}[\bar{\Psi}_1, \bar{\Psi}_2; \boldsymbol{\rho}] = \frac{c^{(2)}}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \times [\nabla_\perp \bar{\Psi}_1(\boldsymbol{\rho}) - \nabla_\perp \bar{\Psi}_2(\boldsymbol{\rho})], \quad (2.67)$$

with $c^{(i)}$ arbitrary complex.

3. Dirac Equation

3.1. CONSTRUCTION OF A FUNDAMENTAL FUNCTIONAL

We now turn to the case of the Dirac equation. The relevant Hamiltonian in Eq. (1.1) is

$$\hat{H} = -ich\boldsymbol{\alpha} \cdot \nabla + \beta mc^2 + V(\mathbf{r}), \quad (3.1)$$

where $\boldsymbol{\alpha}$ and β are standard Dirac matrices, while the wavefunction $\Psi(\mathbf{r})$, obeying $r\Psi(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0$, is a four-component bispinor. We divide the configuration space and the wavefunction in the same way as in section 2 (Fig. 1). Then, Eq. (1.1) is equivalent to equations

$$[\hat{H} - E]\Psi_1(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_1), \quad (3.2)$$

$$[\hat{H} - E]\Psi_2(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_2) \quad (3.3)$$

with

$$r\Psi_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0 \quad (3.4)$$

and

$$\Psi_1(\boldsymbol{\rho}) - \Psi_2(\boldsymbol{\rho}) = 0. \quad (3.5)$$

The starting form of the sought energy functional, taking into account Eqs. (3.2), (3.3), and (3.5), is

$$F[\bar{E}, \bar{\Psi}_1, \bar{\Psi}_2; \bar{\Lambda}_1, \bar{\Lambda}_2, \bar{\lambda}] = \bar{E} + \langle \bar{\Lambda}_1 | [\hat{H} - \bar{E}] \bar{\Psi}_1 \rangle_1 + \langle \bar{\Lambda}_2 | [\hat{H} - \bar{E}] \bar{\Psi}_2 \rangle_2 + (\bar{\lambda} | \bar{\Psi}_1 - \bar{\Psi}_2), \quad (3.6)$$

where \bar{E} , $\bar{\Psi}_i(\mathbf{r})$, $\bar{\Lambda}_i(\mathbf{r})$, and $\bar{\lambda}(\boldsymbol{\rho})$ have the same meaning as in section 2, except that now the functions are bispinors rather than scalars. Volume and surface scalar products are defined as in Eqs. (2.10) and (2.11), respectively, except that now $*$ denotes the Hermitian conjugation. To make the integral over V_2 convergent [cf. also Eq. (3.4)], we require that

$$r\bar{\Psi}_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0, \quad r\bar{\Lambda}_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0. \quad (3.7)$$

The functional (3.6) satisfies

$$F[E, \Psi_1, \Psi_2; \bar{\Lambda}_1, \bar{\Lambda}_2, \bar{\lambda}] = E. \quad (3.8)$$

Employing Eqs. (3.2), (3.3), and (3.5), the first variation of Eq. (3.6) is found to be

$$\begin{aligned} \delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda] = & \delta E[1 - \langle \Lambda_1 | \Psi_1 \rangle_1 \\ & - \langle \Lambda_2 | \Psi_2 \rangle_2] + \langle \Lambda_1 | [\hat{H} - E] \delta \Psi_1 \rangle_1 \\ & + \langle \Lambda_2 | [\hat{H} - E] \delta \Psi_2 \rangle_2 + (\lambda | \delta \Psi_1 - \delta \Psi_2). \end{aligned} \quad (3.9)$$

Since E is real, and since it holds

$$r \Lambda_2(\mathbf{r}) \xrightarrow{r \rightarrow \infty} 0 \quad (3.10)$$

[cf. the second condition in Eq. (3.7)], with the aid of the Gauss divergence formula, which yields

$$\begin{aligned} \langle \Lambda_1 | [\hat{H} - E] \delta \Psi_1 \rangle_1 = & \langle [\hat{H} - E] \Lambda_1 | \delta \Psi_1 \rangle_1 \\ & + c\hbar(i\alpha_{\perp} \Lambda_1 | \delta \Psi_1), \end{aligned} \quad (3.11)$$

$$\begin{aligned} \langle \Lambda_2 | [\hat{H} - E] \delta \Psi_2 \rangle_2 = & \langle [\hat{H} - E] \Lambda_2 | \delta \Psi_2 \rangle_2 \\ & - c\hbar(i\alpha_{\perp} \Lambda_2 | \delta \Psi_2), \end{aligned} \quad (3.12)$$

where

$$\alpha_{\perp}(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho}) \cdot \boldsymbol{\alpha}, \quad (3.13)$$

Eq. (3.9) is transformed into

$$\begin{aligned} \delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda] = & \delta E[1 - \langle \Lambda_1 | \Psi_1 \rangle_1 \\ & - \langle \Lambda_2 | \Psi_2 \rangle_2] + \langle [\hat{H} - E] \Lambda_1 | \delta \Psi_1 \rangle_1 \\ & + \langle [\hat{H} - E] \Lambda_2 | \delta \Psi_2 \rangle_2 + (ich\alpha_{\perp} \Lambda_1 + \lambda | \delta \Psi_1) \\ & - (ich\alpha_{\perp} \Lambda_2 + \lambda | \delta \Psi_2). \end{aligned} \quad (3.14)$$

Demanding that

$$\delta F[E, \Psi_1, \Psi_2; \Lambda_1, \Lambda_2, \lambda] = 0 \quad (3.15)$$

holds for arbitrary δE , $\delta \Psi_1$, and $\delta \Psi_2$, from Eqs. (3.14) and (3.15) we deduce

$$1 - \langle \Lambda_1 | \Psi_1 \rangle_1 - \langle \Lambda_2 | \Psi_2 \rangle_2 = 0, \quad (3.16)$$

$$[\hat{H} - E] \Lambda_1(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_1), \quad (3.17)$$

$$[\hat{H} - E] \Lambda_2(\mathbf{r}) = 0 \quad (\mathbf{r} \in V_2), \quad (3.18)$$

$$ich\alpha_{\perp}(\boldsymbol{\rho}) \Lambda_1(\boldsymbol{\rho}) + \lambda(\boldsymbol{\rho}) = 0, \quad (3.19)$$

and

$$ich\alpha_{\perp}(\boldsymbol{\rho}) \Lambda_2(\boldsymbol{\rho}) + \lambda(\boldsymbol{\rho}) = 0. \quad (3.20)$$

Then, operating on Eqs. (3.19) and (3.20) from the left with $\alpha_{\perp}(\boldsymbol{\rho})$ and making use of the fact that

$$\alpha_{\perp}^2(\boldsymbol{\rho}) = I, \quad (3.21)$$

where I is the unit 4×4 matrix, we find

$$\Lambda_1(\boldsymbol{\rho}) = \Lambda_2(\boldsymbol{\rho}). \quad (3.22)$$

Comparison of Eqs. (3.17), (3.18), (3.22), and (3.10) with Eqs. (3.2), (3.3), (3.5), and (3.4) motivates the choices

$$\Lambda_1(\mathbf{r}) = \eta \Psi_1(\mathbf{r}), \quad (3.23)$$

$$\Lambda_2(\mathbf{r}) = \eta \Psi_2(\mathbf{r}), \quad (3.24)$$

where η is some constant. From Eqs. (3.23), (3.24), and (3.16) this constant is found to be

$$\eta = \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2}, \quad (3.25)$$

hence, we have

$$\Lambda_1(\mathbf{r}) = \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} \Psi_1(\mathbf{r}), \quad (3.26)$$

$$\Lambda_2(\mathbf{r}) = \frac{1}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} \Psi_2(\mathbf{r}). \quad (3.27)$$

Next, let us define the matrices

$$\beta^{(\pm)} = \frac{1}{2}(I \pm \beta), \quad \alpha_{\perp}^{(\pm)}(\boldsymbol{\rho}) = \beta^{(\pm)} \alpha_{\perp}(\boldsymbol{\rho}). \quad (3.28)$$

Premultiplying Eqs. (3.19) and (3.20) with $\beta^{(\pm)}$ and using Eqs. (3.26)–(3.28) yields

$$\beta^{(\pm)} \lambda(\boldsymbol{\rho}) = - \frac{c\hbar}{\langle \Psi_1 | \Psi_1 \rangle_1 + \langle \Psi_2 | \Psi_2 \rangle_2} i\alpha_{\perp}^{(\pm)}(\boldsymbol{\rho}) \Psi_1(\boldsymbol{\rho}), \quad (3.29)$$

$$\beta^{(\pm)\lambda}(\boldsymbol{\rho}) = -\frac{c\hbar}{\langle\Psi_1|\Psi_1\rangle_1 + \langle\Psi_2|\Psi_2\rangle_2} i\alpha_{\perp}^{(\pm)}(\boldsymbol{\rho})\Psi_2(\boldsymbol{\rho}), \quad (3.30)$$

hence, it follows that

$$\beta^{(+)\lambda}(\boldsymbol{\rho}) = -\frac{c\hbar}{\langle\Psi_1|\Psi_1\rangle_1 + \langle\Psi_2|\Psi_2\rangle_2} \times i\alpha_{\perp}^{(+)}(\boldsymbol{\rho})[a\Psi_1(\boldsymbol{\rho}) + (1-a)\Psi_2(\boldsymbol{\rho})], \quad (3.31)$$

$$\beta^{(-)\lambda}(\boldsymbol{\rho}) = -\frac{c\hbar}{\langle\Psi_1|\Psi_1\rangle_1 + \langle\Psi_2|\Psi_2\rangle_2} \times i\alpha_{\perp}^{(-)}(\boldsymbol{\rho})[b\Psi_1(\boldsymbol{\rho}) + (1-b)\Psi_2(\boldsymbol{\rho})] \quad (3.32)$$

with a and b arbitrary complex. From Eqs. (3.31) and (3.32), in virtue of

$$\beta^{(+)} + \beta^{(-)} = I, \quad (3.33)$$

we have

$$\lambda(\boldsymbol{\rho}) = -\frac{c\hbar}{\langle\Psi_1|\Psi_1\rangle_1 + \langle\Psi_2|\Psi_2\rangle_2} \times \{i\alpha_{\perp}^{(+)}(\boldsymbol{\rho})[a\Psi_1(\boldsymbol{\rho}) + (1-a)\Psi_2(\boldsymbol{\rho})] + i\alpha_{\perp}^{(-)}(\boldsymbol{\rho})[b\Psi_1(\boldsymbol{\rho}) + (1-b)\Psi_2(\boldsymbol{\rho})]\}. \quad (3.34)$$

Guided by Eqs. (3.26), (3.27), and (3.34), in the starting functional (3.6), we choose

$$\bar{\Lambda}_1(\mathbf{r}) = \frac{1}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} \bar{\Psi}_1(\mathbf{r}), \quad (3.35)$$

$$\bar{\Lambda}_2(\mathbf{r}) = \frac{1}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} \bar{\Psi}_2(\mathbf{r}), \quad (3.36)$$

$$\bar{\lambda}(\boldsymbol{\rho}) = -\frac{c\hbar}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} \times \{i\alpha_{\perp}^{(+)}(\boldsymbol{\rho})[a\bar{\Psi}_1(\boldsymbol{\rho}) + (1-a)\bar{\Psi}_2(\boldsymbol{\rho})] + i\alpha_{\perp}^{(-)}(\boldsymbol{\rho})[b\bar{\Psi}_1(\boldsymbol{\rho}) + (1-b)\bar{\Psi}_2(\boldsymbol{\rho})]\}. \quad (3.37)$$

This yields the relativistic fundamental functional

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle\bar{\Psi}_1|\hat{H}\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\hat{H}\bar{\Psi}_2\rangle_2}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2}$$

$$-c\hbar \frac{(i\alpha_{\perp}^{(+)}[a\bar{\Psi}_1 + (1-a)\bar{\Psi}_2]|\bar{\Psi}_1 - \bar{\Psi}_2)}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} -c\hbar \frac{(i\alpha_{\perp}^{(-)}[b\bar{\Psi}_1 + (1-b)\bar{\Psi}_2]|\bar{\Psi}_1 - \bar{\Psi}_2)}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2}, \quad (3.38)$$

which does not depend on the energy estimate \bar{E} .

If we employ the Hermitian conjugation property

$$\alpha_{\perp}^{(\pm)*}(\boldsymbol{\rho}) = \alpha_{\perp}^{(\mp)}(\boldsymbol{\rho}), \quad (3.39)$$

the functional (3.38) becomes

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle\bar{\Psi}_1|\hat{H}\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\hat{H}\bar{\Psi}_2\rangle_2}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} -c\hbar \frac{(ai\alpha_{\perp}^{(+)}\bar{\Psi}_1 + [1-a]i\alpha_{\perp}^{(+)}\bar{\Psi}_2|\bar{\Psi}_1 - \bar{\Psi}_2)}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} +c\hbar \frac{(b\bar{\Psi}_1 + [1-b]\bar{\Psi}_2|i\alpha_{\perp}^{(+)}\bar{\Psi}_1 - i\alpha_{\perp}^{(+)}\bar{\Psi}_2)}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} \quad (3.40)$$

or equivalently

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle\bar{\Psi}_1|\hat{H}\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\hat{H}\bar{\Psi}_2\rangle_2}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} -c\hbar \frac{(bi\alpha_{\perp}^{(-)}\bar{\Psi}_1 + [1-b]i\alpha_{\perp}^{(-)}\bar{\Psi}_2|\bar{\Psi}_1 - \bar{\Psi}_2)}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2} +c\hbar \frac{(a\bar{\Psi}_1 + [1-a]\bar{\Psi}_2|i\alpha_{\perp}^{(-)}\bar{\Psi}_1 - i\alpha_{\perp}^{(-)}\bar{\Psi}_2)}{\langle\bar{\Psi}_1|\bar{\Psi}_1\rangle_1 + \langle\bar{\Psi}_2|\bar{\Psi}_2\rangle_2}. \quad (3.41)$$

Structural similarities between the latter two forms of the relativistic fundamental functional and the nonrelativistic equation (2.42) are apparent.

3.2. CONSTRAINED TRIAL FUNCTIONS

At first, consider the particular case when the upper components of the trial functions $\bar{\Psi}_1(\mathbf{r})$ and $\bar{\Psi}_2(\mathbf{r})$ match at the surface \mathcal{S} :

$$\beta^{(+)}\bar{\Psi}_1(\boldsymbol{\rho}) = \beta^{(+)}\bar{\Psi}_2(\boldsymbol{\rho}). \quad (3.42)$$

Operating on both sides of Eq. (3.42) with $i\alpha_{\perp}^{(-)}(\boldsymbol{\rho})$ and employing

$$\alpha_{\perp}^{(\pm)}(\boldsymbol{\rho})\beta^{(\mp)} = \alpha_{\perp}^{(\pm)}(\boldsymbol{\rho}), \quad (3.43)$$

Eq. (3.42) is found to be equivalent to

$$i\alpha_{\perp}^{(-)}(\boldsymbol{\rho})\bar{\Psi}_1(\boldsymbol{\rho}) = i\alpha_{\perp}^{(-)}(\boldsymbol{\rho})\bar{\Psi}_2(\boldsymbol{\rho}). \quad (3.44)$$

Exploiting this relation in Eq. (3.41) reduces the latter to

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - c\hbar \frac{(i\alpha_{\perp}^{(-)}\bar{\Psi}_1 | \bar{\Psi}_1 - \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (3.45)$$

Next, consider the case when the trial functions are forced to match on \mathcal{S} in the lower components:

$$\beta^{(-)}\bar{\Psi}_1(\boldsymbol{\rho}) = \beta^{(-)}\bar{\Psi}_2(\boldsymbol{\rho}). \quad (3.46)$$

This implies

$$i\alpha_{\perp}^{(+)}(\boldsymbol{\rho})\bar{\Psi}_1(\boldsymbol{\rho}) = i\alpha_{\perp}^{(+)}(\boldsymbol{\rho})\bar{\Psi}_2(\boldsymbol{\rho}) \quad (3.47)$$

and from Eq. (3.40) we obtain

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - c\hbar \frac{(i\alpha_{\perp}^{(+)}\bar{\Psi}_1 | \bar{\Psi}_1 - \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (3.48)$$

Finally, if both matching conditions (3.42) and (3.46) are satisfied simultaneously, the functional (3.38) simplifies to

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (3.49)$$

Because of the additivity of integrals, the functional in Eq. (3.49) is identical to the functional (1.3).

3.3. REAL FORM OF THE FUNDAMENTAL FUNCTIONAL

It remains to investigate which conditions should be satisfied in order that the fundamental functional (3.38) possesses the property of being real for arbitrary trial functions:

$$F^*[\bar{\Psi}_1, \bar{\Psi}_2] = F[\bar{\Psi}_1, \bar{\Psi}_2]. \quad (3.50)$$

Taking the complex conjugate of Eq. (3.38) and transforming it with the aid of the Gauss theorem gives

$$F^*[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - c\hbar \frac{(i\alpha_{\perp}^{(-)}[(1-a^*)\bar{\Psi}_1 + a^*\bar{\Psi}_2] | \bar{\Psi}_1)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + c\hbar \frac{(i\alpha_{\perp}^{(-)}[(1-a^*)\bar{\Psi}_1 + a^*\bar{\Psi}_2] | \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - c\hbar \frac{(i\alpha_{\perp}^{(+)}[(1-b^*)\bar{\Psi}_1 + b^*\bar{\Psi}_2] | \bar{\Psi}_1)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + c\hbar \frac{(i\alpha_{\perp}^{(+)}[(1-b^*)\bar{\Psi}_1 + b^*\bar{\Psi}_2] | \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (3.51)$$

Comparing Eqs. (3.51) and (3.38), we see that the property (3.50) will be satisfied for arbitrary $\bar{\Psi}_1$ and $\bar{\Psi}_2$ if, and only if, the constants a and b are related through

$$b = 1 - a^* \quad (3.52)$$

[cf. the nonrelativistic condition (2.52)]. Hence, we infer that the sought real functional is

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - c\hbar \frac{(a i \alpha_{\perp}^{(+)}\bar{\Psi}_1 + [1-a]i\alpha_{\perp}^{(+)}\bar{\Psi}_2 | \bar{\Psi}_1 - \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + c\hbar \frac{([1-a^*]\bar{\Psi}_1 + a^*\bar{\Psi}_2 | i\alpha_{\perp}^{(+)}\bar{\Psi}_1 - i\alpha_{\perp}^{(+)}\bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} \quad (3.53)$$

or, equivalently,

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} - c\hbar \frac{(b i \alpha_{\perp}^{(-)}\bar{\Psi}_1 + [1-b]i\alpha_{\perp}^{(-)}\bar{\Psi}_2 | \bar{\Psi}_1 - \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + c\hbar \frac{([1-b^*]\bar{\Psi}_1 + b^*\bar{\Psi}_2 | i\alpha_{\perp}^{(-)}\bar{\Psi}_1 - i\alpha_{\perp}^{(-)}\bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (3.54)$$

Equations (3.53) and (3.54) should be compared with their nonrelativistic analogue (2.53).

Either of the two forms (3.53) and (3.54) of the real fundamental functional may be used as a starting point for the relativistic generalization of the embedding method [20].

3.4. GENERALIZATION OF THE FUNDAMENTAL FUNCTIONAL

A variety of functionals generalizing the fundamental functional (3.38) may be constructed. The method is completely analogous to that outlined in section 2.4; therefore, the details will not be presented here.

3.5. RELATIONSHIP TO THE WORK OF LOUCKS [4]

With the particular choice

$$a = b = \frac{1}{2} \quad (3.55)$$

the fundamental functional (3.38) becomes

$$F[\bar{\Psi}_1, \bar{\Psi}_2] = \frac{\langle \bar{\Psi}_1 | \hat{H} \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \hat{H} \bar{\Psi}_2 \rangle_2}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2} + \frac{1}{2} c\hbar \frac{(\bar{\Psi}_1 + \bar{\Psi}_2 | i\alpha_{\perp} \bar{\Psi}_1 - i\alpha_{\perp} \bar{\Psi}_2)}{\langle \bar{\Psi}_1 | \bar{\Psi}_1 \rangle_1 + \langle \bar{\Psi}_2 | \bar{\Psi}_2 \rangle_2}. \quad (3.56)$$

This functional, used by Loucks [4] in his investigations on relativistic electronic structure of crystals, is the relativistic analogue of the functional proposed by Schlosser and Marcus [3] and by Brownstein and Zhou [18]. We are not aware of any

published works, other than Ref. [4], that employ discontinuous relativistic trial functions.

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