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A unified construction of variational R-matrix methods: I. The Schrödinger equation

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Abstract. Properties of two linear integral operators $\hat{\mathcal{R}}(E)$ and $\hat{\mathcal{B}}(E) = \hat{\mathcal{R}}^{-1}(E)$, relating function values to normal derivatives on a surface $\mathcal{S}$ of a closed volume $\mathcal{V}$ inside which the function satisfies the Schrödinger equation at energy E, are discussed. Variational principles for matrix elements and eigenvalues of these operators are constructed in a systematic way by using an approach of Gerjuoy *et al*. Some of the variational principles derived were already known in the non-relativistic R-matrix theory of scattering but others seem to be new. Applications of the Rayleigh–Ritz linear trial functions are presented.

1. Introduction

The R-matrix theory [1–8] is one of the most popular techniques used in theoretical studies of atomic, molecular and nuclear processes. In this approach, one divides the configuration space of a considered physical system into several parts and solves a wave equation governing the dynamics of the system separately in each of these domains. The total wavefunction describing the system in the whole configuration space is then obtained by matching solutions obtained in individual regions at common boundaries. All information about a particular domain $\mathcal{V}$ required for the matching process at an enclosing surface $\mathcal{S}$ is embodied in a linear integral energy-dependent operator $\hat{\mathcal{R}}(E)$ which acting at $\mathcal{S}$ on normal derivatives of functions that in $\mathcal{V}$ are solutions of the wave equation at energy E produces values of these functions on $\mathcal{S}$. The goal of the R-matrix theory is to find the operator $\hat{\mathcal{R}}(E)$ either by constructing its kernel or, equivalently, by finding an R-matrix, a matrix representation of the operator $\hat{\mathcal{R}}(E)$ in some functional basis spanning the surface $\mathcal{S}$.

Among various approximate methods of theoretical physics, those based on the variational calculus belong to the most effective [9, 10]. Therefore it is natural to ask whether it would be possible to employ variational methods to achieve the aim of the R-matrix theory. The answer is positive. Already in a classic paper on variational methods of the quantum scattering theory, Kohn [11] proposed a variational principle which was later recognized [1] as a variational principle for an inverse of the R-matrix for a single-channel scattering problem. Shortly afterwards, Jackson [12] derived a restricted variational principle for elements of a multichannel R-matrix. After two decades of stagnation, a revived interest in variational R-matrix methods was caused by Lane and Robson [13], Chatwin [14] and Chatwin and Purcell [15]. Publication of these papers concerning nuclear physics problems

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coincided with the introduction of the R-matrix theory to atomic and molecular physics [16]. Since then the development of the variational R-matrix methods, with very few exceptions [17–20], has been related to the research done in the latter field. Using Kohn's approach, Crawford [21] derived finite-volume variational principles for elements of the scattering and reactance matrices. Although, strictly speaking, these considerations did not concern the R-matrix theory directly, only very slight modifications are necessary to convert Crawford's results into a variational R-matrix method. Oberoi and Nesbet [22, 23] proposed an unrestricted variational principle for elements of the R-matrix and applied it to some model scattering problems. Their work was extended to electron–helium scattering by Kracht and Chang [24]. Zvijac *et al* [25] used the Kohn variational principle to derive a variational correction improving the quality of R-matrix calculations performed with a truncated fixed-boundary condition basis set. Shimamura [26] generalized Jackson's results admitting unrestricted trial functions. The state-of-the-art theory at the end of the seventies was reviewed by Nesbet [27]. The theory received fresh impact when Greene [28] realized that a multichannel version of the Kohn variational principle might be used as a variational principle for reciprocals of eigenvalues of the R-matrix. Importance of this observation was soon recognized and a new effective version of the R-matrix theory based on the Kohn variational principle, the variational eigenchannel R-matrix method, was developed [28–35] and applied to studies of atomic Rydberg states [36–40], atomic and molecular photoionization [28, 30, 34, 41–43] and electron–atom scattering [34, 44] (for a comprehensive review of applications of the eigenchannel approach, see [40]). Further connections between the R-matrix theory and the Kohn variational principle were studied by Altick [45], Manolopoulos and Wyatt [46], Manolopoulos *et al* [47] and Meyer [48]. In addition Nesbet [19, 20, 49] derived variational principles for the operator $\hat{\mathcal{R}}(E)$ and its inverse and applied them to problems in condensed matter and molecular physics.

This brief overview shows that the literature on the variational methods related to the R-matrix theory is quite vast. A reader will also find it very chaotic. Particular variational principles, often closely related, have been developed (or simply guessed) using a wide range of tricks and argumentations. In view of this rather irritating situation, there is a strong desire for a systematic approach to create order out of the present chaos. It appears that such an approach already exists. It was pointed out by Raşeev [41] that the Kohn variational principle for reciprocals of eigenvalues of the R-matrix might be derived by using a general machinery for construction of variational principles exposed by Gerjuoy *et al* [50]. We have found that this machinery may be used to construct, in a systematic fashion, all variational principles related to the R-matrix theory that have already been known and, what we consider to be particularly important, a number of *new* variational principles.

In this paper we present a systematic construction, based on the approach of Gerjuoy *et al* [50], of variational principles related to the R-matrix theory. For the sake of simplicity and clarity, desirable in a paper attempting to unify a variety of somebody else's results, we shall restrict our considerations to the case of a single particle moving in a potential field. Generalization of our results to many-body systems is not difficult and an example of such a generalization, in the context of the electron–atom scattering theory, will be presented elsewhere [51]. In the first part of the paper, presented below, we shall be concerned with a non-relativistic particle whose dynamics is governed by the Schrödinger equation. In the second part [52] we shall derive variational R-matrix methods for a particle described by the Dirac equation.

The plan of the present paper is as follows. In section 2 we define the surface operator $\hat{\mathcal{R}}(E)$ and its inverse $\hat{\mathcal{B}}(E)$ and discuss properties of eigenfunctions of these operators. In

sections 3.1 and 3.2 we derive variational principles for eigenvalues of the operator $\hat{\mathcal{B}}(E)$ and their reciprocals, respectively. In section 3.3 we construct variational principles for matrix elements of the operator $\hat{\mathcal{R}}(E)$ and their reciprocals, while in section 3.4 analogous variational principles for the operator $\hat{\mathcal{B}}(E)$ are derived. In section 4 we discuss restricted forms of the variational principles derived in sections 3.3 and 3.4. Section 5 contains a discussion of applications of the Rayleigh–Ritz linear trial functions in the variational principles obtained in section 3.

2. The operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$

We consider a process governed by the wave equation

$$[\hat{H} - E]\Psi(E, \boldsymbol{r}) = 0 \tag{1}$$

in which a particle of a given real energy E moves in a real, local, spin-independent, in general non-central potential V. In the non-relativistic case discussed in this paper the Hamiltonian $\hat{H}$ has the form

$$\hat{H} = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r}) \tag{2}$$

and the wave equation (1) reads

$$\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(\boldsymbol{r}) - E\right]\Psi(E, \boldsymbol{r}) = 0. \tag{3}$$

In accordance with the philosophy of the R-matrix method, we restrict our considerations to a strictly delimited volume $\mathcal{V}$ enclosed by a surface $\mathcal{S}$ (assumed to consist of a finite number of sufficiently smooth pieces). We wish to find a homogeneous boundary condition satisfied on $\mathcal{S}$ by solutions of equation (1).

Before proceeding further, we establish a notational convention. In the following, $\boldsymbol{r}$ is a position vector of a point in the volume $\mathcal{V}$. If the point $\boldsymbol{r}$ lies on the surface $\mathcal{S}$, we shall denote this using the symbol $\boldsymbol{\rho}$ instead of $\boldsymbol{r}$. To denote volume and surface integrals containing products of two functions, we shall use the following notation

$$\langle f|g\rangle \equiv \int_{\mathcal{V}} \mathrm{d}^3\boldsymbol{r}\, f^*(\boldsymbol{r})g(\boldsymbol{r}) \qquad (f|g) \equiv \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}\, f^*(\boldsymbol{\rho})g(\boldsymbol{\rho}) \tag{4}$$

where the asterisk denotes the complex conjugation. Here $\mathrm{d}^3\boldsymbol{r}$ is an infinitesimal volume element around the point $\boldsymbol{r}$ and $\mathrm{d}^2\boldsymbol{\rho}$ is an infinitesimal *scalar* surface element around the point $\boldsymbol{\rho}$. We also define a surface Dirac delta function $\delta^{(2)}(\boldsymbol{\rho}-\boldsymbol{\rho}')$ so that for any reasonable function $f(\boldsymbol{\rho})$ defined on the surface $\mathcal{S}$ one has

$$\int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \delta^{(2)}(\boldsymbol{\rho} - \boldsymbol{\rho}')f(\boldsymbol{\rho}') = f(\boldsymbol{\rho}). \tag{5}$$

In what follows, we shall denote by $\mathcal{D}(E)$ a set of all solutions of equation (1) corresponding to the fixed *real* energy E. Similarly, we shall denote by $\mathcal{D}_{\mathcal{S}}(E)$ a set of surface parts of functions belonging to $\mathcal{D}(E)$. In other words, if the function $\Psi(E, \boldsymbol{r})$ is from $\mathcal{D}(E)$, then the surface function $\Psi(E, \boldsymbol{\rho})$ is in $\mathcal{D}_{\mathcal{S}}(E)$. Let $\Psi(E, \boldsymbol{r})$ and $\Psi'(E, \boldsymbol{r})$ be two arbitrary functions from $\mathcal{D}(E)$. Applying the Green integration theorem we have

$$\langle \hat{H}\Psi'|\Psi\rangle - \langle \Psi'|\hat{H}\Psi\rangle = \frac{\hbar^2}{2m}(\Psi'|\nabla_n\Psi) - \frac{\hbar^2}{2m}(\nabla_n\Psi'|\Psi) \tag{6}$$

where $\nabla_n\Psi(E,\boldsymbol{\rho})$ denotes the outward normal derivative of the function $\Psi(E,\boldsymbol{r})$ at the surface point $\boldsymbol{\rho}$. In virtue of the reality of E the left-hand side of this equation vanishes yielding

$$(\Psi'|\nabla_n\Psi) = (\nabla_n\Psi'|\Psi). \tag{7}$$

In equation (7) it may be formally interpreted that the normal derivative operator ∇_n, when acting on functions from $\mathcal{D}_{\mathcal{S}}(E)$, is Hermitean with respect to the surface scalar product $(|)$.

To proceed further we observe that since any linear operator on the domain $\mathcal{D}_{\mathcal{S}}(E)$ may be represented by some integral operator, we have

$$\nabla_n\Psi(E,\boldsymbol{\rho}) = \hat{\mathcal{B}}(E)\Psi(E,\boldsymbol{\rho}) \tag{8}$$

or equivalently

$$\nabla_n\Psi(E,\boldsymbol{\rho}) = \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')\Psi(E,\boldsymbol{\rho}') \tag{9}$$

where $\hat{\mathcal{B}}(E)$ is a Hermitean integral operator defined on the surface $\mathcal{S}$ and

$$\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \mathcal{B}^*(E,\boldsymbol{\rho}',\boldsymbol{\rho}) \tag{10}$$

is an associated Hermitean integral kernel. It must be emphasized that the operators ∇_n and $\hat{\mathcal{B}}(E)$ are *not* identical since for an arbitrary function $\Phi(\boldsymbol{r})$, in general, we have

$$\nabla_n\Phi(\boldsymbol{\rho}) \neq \hat{\mathcal{B}}(E)\Phi(\boldsymbol{\rho}) \tag{11}$$

unless $\Phi(\boldsymbol{r})$ is from $\mathcal{D}(E)$. In applications, instead of the kernel $\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$, it is customary to use a kernel $\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ associated with the operator $\hat{\mathcal{R}}(E) = \hat{\mathcal{B}}^{-1}(E)$. For any function $\Psi(E,\boldsymbol{r})$ from $\mathcal{D}(E)$ we have on the surface $\mathcal{S}$

$$\Psi(E,\boldsymbol{\rho}) = \hat{\mathcal{R}}(E)\nabla_n\Psi(E,\boldsymbol{\rho}) \tag{12}$$

or equivalently

$$\Psi(E,\boldsymbol{\rho}) = \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}')\nabla_n\Psi(E,\boldsymbol{\rho}'). \tag{13}$$

Since the operator $\hat{\mathcal{R}}(E)$ is the inverse of the operator $\hat{\mathcal{B}}(E)$, the kernels $\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ and $\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ are reciprocal in the sense of

$$\int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}''\, \mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}'')\mathcal{B}(E,\boldsymbol{\rho}'',\boldsymbol{\rho}') = \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}''\, \mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}'')\mathcal{R}(E,\boldsymbol{\rho}'',\boldsymbol{\rho}') = \delta^{(2)}(\boldsymbol{\rho}-\boldsymbol{\rho}'). \tag{14}$$

By virtue of the Hermicity of $\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ the kernel $\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ is also Hermitean

$$\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \mathcal{R}^*(E,\boldsymbol{\rho}',\boldsymbol{\rho}). \tag{15}$$

Let $\{\Phi_i(\boldsymbol{\rho})\}$ be an orthonormal, in the sense of the surface scalar product $(|)$, basis set spanning the surface $\mathcal{S}$. In this basis the kernels $\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ and $\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ have expansions

$$\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_{\text{all } i,\,j} \Phi_i(\boldsymbol{\rho})(\Phi_i|\hat{\mathcal{B}}\Phi_j)\Phi_j^*(\boldsymbol{\rho}') \tag{16}$$

$$\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_{\text{all } i,\,j} \Phi_i(\boldsymbol{\rho})(\Phi_i|\hat{\mathcal{R}}\Phi_j)\Phi_j^*(\boldsymbol{\rho}') \tag{17}$$

where the matrix elements

$$(\Phi_i|\hat{\mathcal{B}}\Phi_j) \equiv \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho} \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \Phi_i^*(\boldsymbol{\rho})\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')\Phi_j(\boldsymbol{\rho}') \tag{18}$$

and

$$(\Phi_i|\hat{\mathcal{R}}\Phi_j) \equiv \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho} \int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \Phi_i^*(\boldsymbol{\rho})\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')\Phi_j(\boldsymbol{\rho}') \tag{19}$$

form Hermitean matrices $\mathbf{B}(E)$ and $\mathbf{R}(E) = \mathbf{B}^{-1}(E)$, respectively. The matrix $\mathbf{R}(E)$ is called the R-matrix for equation (1) in the representation $\{\Phi_i(\boldsymbol{\rho})\}$.

Consider now a set of those functions $\{\Psi_i(E, \boldsymbol{r})\}$ from $\mathcal{D}(E)$ that have constant logarithmic normal derivatives on the surface $\mathcal{S}$

$$\nabla_n \Psi_i(E, \boldsymbol{\rho}) - b_i(E)\Psi_i(E, \boldsymbol{\rho}) = 0 \tag{20}$$

(apart from possible incidental degeneracies, the constants $b_i(E)$ will differ for different functions $\Psi_i(E, \boldsymbol{r})$). Because of equation (8), we may equivalently write

$$\hat{\mathcal{B}}(E)\Psi_i(E, \boldsymbol{\rho}) - b_i(E)\Psi_i(E, \boldsymbol{\rho}) = 0. \tag{21}$$

In equation (21) it may be interpreted that the surface functions $\{\Psi_i(E, \boldsymbol{\rho})\}$ are eigenfunctions of the operator $\hat{\mathcal{B}}(E)$ and that $\{b_i(E)\}$ are corresponding eigenvalues. Since the operator $\hat{\mathcal{B}}(E)$ is Hermitean, its eigenvalues are real and eigenfunctions corresponding to different eigenvalues are orthogonal over the surface $\mathcal{S}$. In what follows, we shall assume that they are normalized to unity over the surface $\mathcal{S}$ and that eigenfunctions corresponding to degenerate eigenvalues (if such exist) are also mutually orthogonal. Then for two arbitrary eigenfunctions of $\hat{\mathcal{B}}(E)$ one has

$$(\Psi_i|\Psi_j) = \delta_{ij}. \tag{22}$$

The eigenfunctions $\{\Psi_i(E, \boldsymbol{\rho})\}$ form a complete set spanning the surface $\mathcal{S}$ and with the normalization (22) the corresponding closure relation is

$$\sum_{\text{all } i} \Psi_i(E, \boldsymbol{\rho})\Psi_i^*(E, \boldsymbol{\rho}') = \delta^{(2)}(\boldsymbol{\rho} - \boldsymbol{\rho}'). \tag{23}$$

With the help of the eigenfunctions $\{\Psi_i(E, \boldsymbol{\rho})\}$ and the corresponding eigenvalues $\{b_i(E)\}$ we may reconstruct the kernels $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ and $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$. Indeed, by virtue of equations (9) and (20) we have

$$\int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')\Psi_i(E, \boldsymbol{\rho}') = b_i(E)\Psi_i(E, \boldsymbol{\rho}) \tag{24}$$

which implies a spectral representation of the kernel $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$

$$\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{\text{all } i} \Psi_i(E, \boldsymbol{\rho})b_i(E)\Psi_i^*(E, \boldsymbol{\rho}'). \tag{25}$$

Similarly, for the kernel $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ we have the eigenvalue equation

$$\int_{\mathcal{S}} \mathrm{d}^2\boldsymbol{\rho}'\, \mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')\Psi_i(E, \boldsymbol{\rho}') = b_i^{-1}(E)\Psi_i(E, \boldsymbol{\rho}) \tag{26}$$

and the spectral expansion

$$\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{\text{all } i} \Psi_i(E, \boldsymbol{\rho})b_i^{-1}(E)\Psi_i^*(E, \boldsymbol{\rho}'). \tag{27}$$

3. Construction of variational principles

3.1. The variational principle for eigenvalues of $\hat{\mathcal{B}}(E)$

In this subsection we shall attempt to solve the following problem: find variational estimates of eigenvalues of the operator $\hat{\mathcal{B}}(E)$, the real quantities defined directly by equations (20) and (21) and indirectly (because these equations contain $\Psi_i(E, \boldsymbol{\rho})$ and its normal derivative) by equation (1). This is the variational problem with constraints and may be solved by using the Lagrange method of undetermined multipliers. Following the suggestion of Raşeev [41], we use the general recipe of Gerjuoy *et al* [50] and construct a functional (for the sake of brevity, hereafter we shall omit indices at eigenvalues, eigenfunctions and related quantities)

$$F[\overline{b}, \overline{\lambda}, \overline{\Lambda}, \overline{\Psi}] = \overline{b} + (\overline{\lambda}|\nabla_n\overline{\Psi} - \overline{b}\,\overline{\Psi}) + \langle\overline{\Lambda}|[\hat{H} - E]\overline{\Psi}\rangle. \tag{28}$$

Here $\overline{b}$ is some number (not necessarily real), $\overline{\lambda}(\boldsymbol{\rho})$ is an arbitrary well behaving function defined on the surface $\mathcal{S}$ while $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Lambda}(\boldsymbol{r})$ are arbitrary well behaving functions defined in $\mathcal{V}$. The auxiliary functions $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ play a role of Lagrange multipliers (or, more correctly, Lagrange functions) incorporating the constraints (20) and (1), respectively. If $\overline{\Psi}(\boldsymbol{r})$ coincides with the eigenchannel function $\Psi(E, \boldsymbol{r})$ and if $\overline{b}$ simultenously equals the corresponding logarithmic derivative $b(E)$, then

$$F[b(E), \overline{\lambda}, \overline{\Lambda}, \Psi] = b(E) \tag{29}$$

irrespective of the forms of the Lagrange functions $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$. According to Gerjuoy *et al* [50], there exist such functions $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$ that the functional (28) is stationary for small arbitrary variations of $\overline{b}$ and $\overline{\Psi}(\boldsymbol{r})$ around $b(E)$ and $\Psi(E, \boldsymbol{r})$,

$$\delta b = \overline{b} - b(E) \qquad \delta\Psi(\boldsymbol{r}) = \overline{\Psi}(\boldsymbol{r}) - \Psi(E, \boldsymbol{r}) \tag{30}$$

and small arbitrary variations of the Lagrange functions $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ around $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$,

$$\delta\lambda(\boldsymbol{\rho}) = \overline{\lambda}(\boldsymbol{\rho}) - \lambda(\boldsymbol{\rho}) \qquad \delta\Lambda(\boldsymbol{r}) = \overline{\Lambda}(\boldsymbol{r}) - \Lambda(\boldsymbol{r}) \tag{31}$$

i.e.

$$\delta F[b, \lambda, \Lambda, \Psi] = 0. \tag{32}$$

We shall find the functions $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$ and show that they are closely related to the eigenfunction $\Psi(E, \boldsymbol{r})$. We have

$$\begin{aligned}\delta F[b, \lambda, \Lambda, \Psi] = {} & \delta b + (\delta\lambda|\nabla_n\Psi - b\Psi) - \delta b(\lambda|\Psi) + (\lambda|\nabla_n\delta\Psi - b\delta\Psi) \\ & + \langle\delta\Lambda|[\hat{H} - E]\Psi\rangle + \langle\Lambda|[\hat{H} - E]\delta\Psi\rangle.\end{aligned} \tag{33}$$

Because of equations (20) and (1), the second and fifth terms on the right-hand side vanish and equation (33) simplifies to the form

$$\delta F[b, \lambda, \Lambda, \Psi] = \delta b[1 - (\lambda|\Psi)] + (\lambda|\nabla_n\delta\Psi - b\delta\Psi) + \langle\Lambda|[\hat{H} - E]\delta\Psi\rangle. \tag{34}$$

With the aid of the Green integration theorem, the last term on the right-hand side of this equation may be transformed in the following way

$$\langle\Lambda|[\hat{H} - E]\delta\Psi\rangle = \langle[\hat{H} - E]\Lambda|\delta\Psi\rangle + \frac{\hbar^2}{2m}(\nabla_n\Lambda|\delta\Psi) - \frac{\hbar^2}{2m}(\Lambda|\nabla_n\delta\Psi) \tag{35}$$

and this allows us to rewrite the first variation of the functional (28) as

$$\begin{aligned}\delta F[b, \lambda, \Lambda, \Psi] = {} & \delta b[1 - (\lambda|\Psi)] + \left(\frac{\hbar^2}{2m}\nabla_n\Lambda - b\lambda\middle|\delta\Psi\right) \\ & + \left(\lambda - \frac{\hbar^2}{2m}\Lambda\middle|\nabla_n\delta\Psi\right) + \langle[\hat{H} - E]\Lambda|\delta\Psi\rangle.\end{aligned} \tag{36}$$

In view of the arbitrariness of δb, $\delta\Psi(\boldsymbol{r})$ and $\nabla_n\delta\Psi(\boldsymbol{\rho})$, from equations (32) and (36) we have

$$1-(\lambda|\Psi)=0 \tag{37}$$

$$[\hat{H}-E]\Lambda(\boldsymbol{r})=0 \qquad \text{in } \mathcal{V} \tag{38}$$

$$\lambda(\boldsymbol{\rho})-\frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho})=0 \qquad \text{on } \mathcal{S} \tag{39}$$

and

$$\frac{\hbar^2}{2m}\nabla_n\Lambda(\boldsymbol{\rho})-b(E)\lambda(\boldsymbol{\rho})=0 \qquad \text{on } \mathcal{S}. \tag{40}$$

From the last two equations one has

$$\nabla_n\Lambda(\boldsymbol{\rho})-b(E)\Lambda(\boldsymbol{\rho})=0 \tag{41}$$

$$\lambda(\boldsymbol{\rho})=\frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho}). \tag{42}$$

It follows from equations (38) and (41) that the function $\Lambda(\boldsymbol{r})$ satisfies exactly the same equation in $\mathcal{V}$ and the same boundary condition on $\mathcal{S}$ as the eigenfunction $\Psi(E,\boldsymbol{r})$ does and therefore one may *choose*

$$\Lambda(\boldsymbol{r})=\gamma\Psi(E,\boldsymbol{r}) \tag{43}$$

where γ is a constant and is to be determined. (That this is indeed our *choice* is illustrated by the fact that a time-reversed function $\hat{T}\Psi(E,\boldsymbol{r})$, where $\hat{T}$ is the time-reversal operator, also satisfies the Schrödinger equation (1) and the boundary condition (20).) To find γ we utilize equation (42) and the condition (37) obtaining

$$\gamma=\frac{2m}{\hbar^2}\frac{1}{(\Psi|\Psi)} \tag{44}$$

hence

$$\Lambda(\boldsymbol{r})=\frac{2m}{\hbar^2}\frac{1}{(\Psi|\Psi)}\Psi(E,\boldsymbol{r}) \tag{45}$$

and

$$\lambda(\boldsymbol{\rho})=\frac{1}{(\Psi|\Psi)}\Psi(E,\boldsymbol{\rho}). \tag{46}$$

The relations (45) and (46) allow us to reduce a number of arguments of the functional (28). Let us *choose* a class of Lagrange functions $\bar{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ such that

$$\overline{\Lambda}(\boldsymbol{r})=\frac{2m}{\hbar^2}\frac{1}{(\overline{\Psi}|\overline{\Psi})}\overline{\Psi}(\boldsymbol{r}) \tag{47}$$

$$\bar{\lambda}(\boldsymbol{\rho})=\frac{1}{(\overline{\Psi}|\overline{\Psi})}\overline{\Psi}(\boldsymbol{\rho}). \tag{48}$$

With this natural choice the functional (28) becomes

$$F[\overline{\Psi}]=\frac{(\overline{\Psi}|\nabla_n\overline{\Psi})}{(\overline{\Psi}|\overline{\Psi})}+\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}\rangle}{(\overline{\Psi}|\overline{\Psi})}. \tag{49}$$

As follows from the method of its construction, this functional is stationary for small arbitrary variations of $\overline{\Psi}(\boldsymbol{r})$ about $\Psi(E,\boldsymbol{r})$ and its stationary value is $b(E)$. We also observe

that application of the Green integration theorem to the volume integral in equation (49) gives

$$F[\overline{\Psi}] = \frac{(\nabla_n\overline{\Psi}|\overline{\Psi})}{(\overline{\Psi}|\overline{\Psi})} + \frac{2m}{\hbar^2}\frac{\langle[\hat{H}-E]\overline{\Psi}|\overline{\Psi}\rangle}{(\overline{\Psi}|\overline{\Psi})}. \tag{50}$$

Comparison of this equation with equation (49) shows that

$$F[\overline{\Psi}] = F^*[\overline{\Psi}] \tag{51}$$

i.e. the functional (49) is real for any trial function $\overline{\Psi}(\boldsymbol{r})$. This is a desirable property since the value of this functional is an estimate of the real quantity $b(E)$.

Summarizing, we have the following unrestricted variational principle for eigenvalues of the operator $\hat{\mathcal{B}}(E)$

$$b(E) = \text{stat}\left\{\frac{(\overline{\Psi}|\nabla_n\overline{\Psi})}{(\overline{\Psi}|\overline{\Psi})} + \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}\rangle}{(\overline{\Psi}|\overline{\Psi})}\right\}. \tag{52}$$

Equation (52) is the celebrated Kohn variational principle [11] and has been extensively used in variational eigenchannel R-matrix calculations in atomic physics [28–44].

3.2. The variational principle for eigenvalues of $\hat{\mathcal{R}}(E)$

In this subsection we shall derive a functional whose stationary values are eigenvalues of the operator $\hat{\mathcal{R}}(E)$. The derivation is based on the observations that eigenvalues of $\hat{\mathcal{R}}(E)$ are reciprocals of eigenvalues of $\hat{\mathcal{B}}(E)$ and that the boundary condition (20) may be rewritten in the form

$$\nabla_n\Psi(E,\boldsymbol{\rho}) - [b^{-1}(E)]^{-1}\Psi(E,\boldsymbol{\rho}) = 0. \tag{53}$$

Consider a functional

$$F[\overline{b^{-1}},\overline{\lambda},\overline{\Lambda},\overline{\Psi}] = \overline{b^{-1}} + (\overline{\lambda}|\nabla_n\overline{\Psi} - (\overline{b^{-1}})^{-1}\overline{\Psi}) + \langle\overline{\Lambda}|[\hat{H}-E]\overline{\Psi}\rangle \tag{54}$$

where $\overline{b^{-1}}$ is some number, $\overline{\lambda}(\boldsymbol{\rho})$ is a sufficiently regular function defined on the surface $\mathcal{S}$ while $\overline{\Lambda}(\boldsymbol{r})$ and $\overline{\Psi}(\boldsymbol{r})$ are sufficiently regular functions defined in the volume $\mathcal{V}$. The auxiliary functions $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ are Lagrange functions for the problem at hand and incorporate the constraints (53) and (1) defining eigenvalues $b(E)$ and eigenfunctions $\Psi(E,\boldsymbol{r})$. The first variation of the functional (54) produced by small variations of its arguments around $b^{-1}(E)$, $\lambda(\boldsymbol{\rho})$, $\Lambda(\boldsymbol{r})$ and $\Psi(E,\boldsymbol{r})$, respectively, is

$$\delta F[b^{-1},\lambda,\Lambda,\Psi] = \delta b^{-1} + \delta b^{-1}b^2(\lambda|\Psi) + (\lambda|\nabla_n\delta\Psi - b\delta\Psi) + \langle\Lambda|[\hat{H}-E]\delta\Psi\rangle \tag{55}$$

(here δb^{-1} means $\delta(b^{-1})$ and *not* $(\delta b)^{-1}$) and, after application of the Green formula, may be rewritten as

$$\begin{aligned}\delta F[b^{-1},\lambda,\Lambda,\Psi] = {} & \delta b^{-1}[1+b^2(\lambda|\Psi)] + \left(\frac{\hbar^2}{2m}\nabla_n\Lambda - b\lambda\middle|\delta\Psi\right) \\ & + \left(\lambda - \frac{\hbar^2}{2m}\Lambda\middle|\nabla_n\delta\Psi\right) + \langle[\hat{H}-E]\Lambda|\delta\Psi\rangle.\end{aligned} \tag{56}$$

We stipulate that the functional (54) should be stationary for small variations of its arguments around their sought forms

$$\delta F[b^{-1},\lambda,\Lambda,\Psi] = 0 \tag{57}$$

hence, one obtains

$$1 + b^2(E)(\lambda|\Psi) = 0 \tag{58}$$

$$[\hat{H} - E]\Lambda(\boldsymbol{r}) = 0 \qquad \text{in } \mathcal{V} \tag{59}$$

$$\frac{\hbar^2}{2m}\nabla_n\Lambda(\boldsymbol{\rho}) - b(E)\lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{60}$$

and

$$\lambda(\boldsymbol{\rho}) - \frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S}. \tag{61}$$

Equations (60) and (61) give

$$\nabla_n\Lambda(\boldsymbol{\rho}) - b(E)\Lambda(\boldsymbol{\rho}) = 0 \tag{62}$$

and

$$\lambda(\boldsymbol{\rho}) = \frac{\hbar^2}{2m}b^{-1}(E)\nabla_n\Lambda(\boldsymbol{\rho}). \tag{63}$$

Comparison of equations (59) and (62) with equations (1) and (20) shows that the Lagrange function $\Lambda(\boldsymbol{r})$ may be chosen in the form

$$\Lambda(\boldsymbol{r}) = \gamma\Psi(E, \boldsymbol{r}) \tag{64}$$

where the constant γ is to be determined. After utilizing equations (58), (61) and (64) one finds

$$\gamma = -\frac{2m}{\hbar^2}b^{-2}(E)\frac{1}{(\Psi|\Psi)} = -\frac{2m}{\hbar^2}\frac{1}{(\nabla_n\Psi|\nabla_n\Psi)} \tag{65}$$

hence

$$\Lambda(\boldsymbol{r}) = -\frac{2m}{\hbar^2}\frac{1}{(\nabla_n\Psi|\nabla_n\Psi)}\Psi(E, \boldsymbol{r}) \tag{66}$$

and, from equations (63) and (66),

$$\lambda(\boldsymbol{\rho}) = -\frac{(\Psi|\Psi)}{(\Psi|\nabla_n\Psi)(\nabla_n\Psi|\nabla_n\Psi)}\nabla_n\Psi(E, \boldsymbol{\rho}) \tag{67}$$

where we have made use of the fact that

$$b^{-1}(E) = \frac{(\Psi|\Psi)}{(\Psi|\nabla_n\Psi)} = \frac{(\Psi|\Psi)}{(\nabla_n\Psi|\Psi)}. \tag{68}$$

Now let us assume that $\overline{b^{-1}}$ is given by

$$\overline{b^{-1}} = \frac{(\overline{\Psi}|\overline{\Psi})}{(\nabla_n\overline{\Psi}|\overline{\Psi})} \tag{69}$$

and let us restrict ourselves to those Lagrange functions $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ that may be written as

$$\overline{\lambda}(\boldsymbol{\rho}) = -\frac{(\overline{\Psi}|\overline{\Psi})}{(\overline{\Psi}|\nabla_n\overline{\Psi})(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}\nabla_n\overline{\Psi}(\boldsymbol{\rho}) \tag{70}$$

$$\overline{\Lambda}(\boldsymbol{r}) = -\frac{2m}{\hbar^2}\frac{1}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}\overline{\Psi}(\boldsymbol{r}). \tag{71}$$

Two comments are appropriate here. First, in general, the estimate (69) of $b^{-1}(E)$ will not be real although the latter quantity is real itself. Secondly, if the trial function $\overline{\Psi}(\boldsymbol{r})$ differs from the eigenfunction $\Psi(E, \boldsymbol{r})$ by a first-order quantity (i.e. if it is a reasonable

estimate of $\Psi(E,\boldsymbol{r})$), then it is clear that $\overline{b^{-1}}$, $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ defined above also differ from $b^{-1}(E)$, $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$ defined, respectively, by equations (68), (67) and (66) by first-order quantities. Substitution of the particular forms (69)–(71) of $\overline{b^{-1}}$, $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ into equation (54) gives

$$F[\overline{\Psi}]=\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}-\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}\rangle}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}. \tag{72}$$

The same functional will be obtained if, instead of $\overline{b^{-1}}$ defined by equation (69), we use

$$\overline{b^{-1}}=\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})} \tag{73}$$

and the Lagrange functions (70) and (71). Moreover, making use of the Green theorem to transform the right-hand side of equation (72), we obtain

$$F[\overline{\Psi}]=\frac{(\overline{\Psi}|\nabla_n\overline{\Psi})}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}-\frac{2m}{\hbar^2}\frac{\langle[\hat{H}-E]\overline{\Psi}|\overline{\Psi}\rangle}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})} \tag{74}$$

and comparison of this equation with equation (72) shows that the functional $F[\overline{\Psi}]$ derived is real for any trial function $\overline{\Psi}$,

$$F[\overline{\Psi}]=F^*[\overline{\Psi}]. \tag{75}$$

Thus, we have the variational principle for eigenvalues of the operator $\hat{\mathcal{R}}(E)$ (reciprocals of eigenvalues of the operator $\hat{\mathcal{B}}(E)$)

$$b^{-1}(E)=\operatorname{stat}\left\{\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}-\frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}\rangle}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}\right\}. \tag{76}$$

Equation (76) is an analogue of the Kohn variational principle (52) derived in the preceding subsection.

3.3. The variational principles for matrix elements of $\hat{\mathcal{R}}(E)$ and their reciprocals

In this subsection we shall derive variational principles for matrix elements of the operator $\hat{\mathcal{R}}(E)$ between two sufficiently regular functions $\Phi(\boldsymbol{\rho})$ and $\Phi'(\boldsymbol{\rho})$ defined on the surface $\mathcal{S}$. To this end we introduce two functions $\Psi(E,\boldsymbol{r})$ and $\Psi'(E,\boldsymbol{r})$ from $\mathcal{D}(E)$ satisfying on the surface $\mathcal{S}$ *inhomogeneous Neumann* boundary conditions

$$\nabla_n\Psi(E,\boldsymbol{\rho})=\Phi(\boldsymbol{\rho})\qquad\nabla_n\Psi'(E,\boldsymbol{\rho})=\Phi'(\boldsymbol{\rho}). \tag{77}$$

(The functions $\Psi(E,\boldsymbol{r})$ used throughout this and the following subsections have nothing whatever to do with eigenfunctions of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ denoted in the two preceding subsections with the same symbols.) Since the functions $\Psi(E,\boldsymbol{r})$ and $\Psi'(E,\boldsymbol{r})$ belong to $\mathcal{D}(E)$, equations (77) may be equivalently rewritten in the form

$$\Psi(E,\boldsymbol{\rho})=\hat{\mathcal{R}}(E)\Phi(\boldsymbol{\rho})\qquad\Psi'(E,\boldsymbol{\rho})=\hat{\mathcal{R}}(E)\Phi'(\boldsymbol{\rho}). \tag{78}$$

Our aim is to construct a functional whose stationary value is $(\Phi|\hat{\mathcal{R}}\Phi')$. We shall treat equations (1), (77) and (78) as constraints and seek the functional in the form

$$\begin{aligned}F[\Phi,\Phi';\hat{\overline{\mathcal{R}}},\overline{\chi},\overline{\lambda},\overline{\Lambda},\overline{\Psi}']&=(\Phi|\hat{\overline{\mathcal{R}}}\Phi')+(\overline{\chi}|\overline{\Psi}'-\hat{\overline{\mathcal{R}}}\Phi')\\&\quad+(\overline{\lambda}|\nabla_n\overline{\Psi}'-\Phi')+\langle\overline{\Lambda}|[\hat{H}-E]\overline{\Psi}'\rangle.\end{aligned} \tag{79}$$

Here $\hat{\overline{\mathcal{R}}}$ is some operator (*not* necessarily Hermitean) acting on functions defined on the surface $\mathcal{S}$, $\overline{\chi}(\boldsymbol{\rho})$ and $\overline{\lambda}(\boldsymbol{\rho})$ are well behaving and otherwise completely arbitrary functions

defined on the surface $\mathcal{S}$, while $\overline{\Psi}'(\boldsymbol{r})$ and $\overline{\Lambda}(\boldsymbol{r})$ are arbitrary well behaving functions defined in $\mathcal{V}$. The functions $\overline{\chi}(\boldsymbol{\rho})$, $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ are Lagrange functions for the problem under consideration. Suppose now that the functional (79) is subjected to small arbitrary variations of its arguments. The first variation of the functional is

$$\delta F[\Phi, \Phi'; \hat{\mathcal{R}}, \chi, \lambda, \Lambda, \Psi'] = (\Phi|\delta\hat{\mathcal{R}}\Phi') + (\chi|\delta\Psi' - \delta\hat{\mathcal{R}}\Phi') + (\lambda|\nabla_n\delta\Psi') + \langle\Lambda|[\hat{H} - E]\delta\Psi'\rangle \tag{80}$$

where we have utilized the fact that terms containing variations $\delta\chi(\boldsymbol{\rho})$, $\delta\lambda(\boldsymbol{\rho})$ and $\delta\Lambda(\boldsymbol{r})$ must vanish if the constraints (1), (77) and (78) are to be satisfied. Application of the Green theorem to the last term on the right-hand side of equation (80) allows us to rewrite the first variation of the functional in the form

$$\delta F[\Phi, \Phi'; \hat{\mathcal{R}}, \chi, \lambda, \Lambda, \Psi'] = (\Phi - \chi|\delta\hat{\mathcal{R}}\Phi') + \left(\chi + \frac{\hbar^2}{2m}\nabla_n\Lambda\middle|\delta\Psi'\right) + \left(\lambda - \frac{\hbar^2}{2m}\Lambda\middle|\nabla_n\delta\Psi'\right) + \langle[\hat{H} - E]\Lambda|\delta\Psi'\rangle. \tag{81}$$

On stipulating

$$\delta F[\Phi, \Phi'; \hat{\mathcal{R}}, \chi, \lambda, \Lambda, \Psi'] = 0 \tag{82}$$

we obtain

$$[\hat{H} - E]\Lambda(\boldsymbol{r}) = 0 \qquad \text{in } \mathcal{V} \tag{83}$$

$$\Phi(\boldsymbol{\rho}) - \chi(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{84}$$

$$\chi(\boldsymbol{\rho}) + \frac{\hbar^2}{2m}\nabla_n\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{85}$$

and

$$\lambda(\boldsymbol{\rho}) - \frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{86}$$

hence, it follows that

$$\chi(\boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \tag{87}$$

and

$$\nabla_n\Lambda(\boldsymbol{\rho}) = -\frac{2m}{\hbar^2}\Phi(\boldsymbol{\rho}). \tag{88}$$

Equations (83) and (88) show that the function $\Lambda(\boldsymbol{r})$ satisfies the same equation in the volume $\mathcal{V}$ as the wavefunction $\Psi(E, \boldsymbol{r})$ does, and the inhomogeneous Neumann boundary condition which differs from the boundary condition (77) satisfied by the latter function only by the multiplicative factor $-2m/\hbar^2$ in the inhomogeneous term. This implies that we may choose $\Lambda(\boldsymbol{r})$ in the form

$$\Lambda(\boldsymbol{r}) = -\frac{2m}{\hbar^2}\Psi(E, \boldsymbol{r}) \tag{89}$$

and consequently (cf equation (86))

$$\lambda(\boldsymbol{\rho}) = -\Psi(E, \boldsymbol{\rho}). \tag{90}$$

Let us restrict our discussion to those Lagrange functions $\overline{\chi}(\boldsymbol{\rho})$, $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ which may be written in the forms

$$\overline{\chi}(\boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \tag{91}$$

$$\overline{\lambda}(\boldsymbol{\rho}) = -\overline{\Psi}(\boldsymbol{\rho}) \tag{92}$$

and

$$\overline{\Lambda}(\boldsymbol{r}) = -\frac{2m}{\hbar^2}\overline{\Psi}(\boldsymbol{r}). \tag{93}$$

It is clear that if the functions $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ differ from $\Psi(E,\boldsymbol{r})$ and $\Psi'(E,\boldsymbol{r})$ by first-order quantities, the Lagrange functions $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ defined above will also differ from $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$ defined, respectively, by equations (90) and (89), by first-order quantities. Substituting these particular forms of the Lagrange functions to equation (79) we obtain the functional

$$F[\Phi,\Phi';\overline{\Psi},\overline{\Psi}'] = (\Phi|\overline{\Psi}') + (\overline{\Psi}|\Phi') - (\overline{\Psi}|\nabla_n\overline{\Psi}') - \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle. \tag{94}$$

By applying the Green theorem to the volume integral appearing on the right-hand side of the above formula, it may be easily verified that the functional (94) possesses a symmetry property

$$F[\Phi,\Phi';\overline{\Psi},\overline{\Psi}'] = F^*[\Phi',\Phi;\overline{\Psi}',\overline{\Psi}]. \tag{95}$$

This functional is stationary for small but otherwise arbitrary variations of $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ around $\Psi(E,\boldsymbol{r})$ and $\Psi'(E,\boldsymbol{r})$, respectively, and its stationary value is $(\Phi|\hat{\mathcal{R}}\Phi')$. Therefore, we have the variational principle

$$(\Phi|\hat{\mathcal{R}}\Phi') = \text{stat}\left\{(\Phi|\overline{\Psi}') + (\overline{\Psi}|\Phi') - (\overline{\Psi}|\nabla_n\overline{\Psi}') - \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle\right\}. \tag{96}$$

It was derived previously, in an entirely different way, by Shimamura [26].

We may also attempt to construct a variational principle for $(\Phi|\hat{\mathcal{R}}\Phi')^{-1}$. To this end we treat equations (1), (77) and (78) as constraints and consider a functional

$$\begin{aligned} F[\Phi,\Phi';\hat{\overline{\mathcal{R}}},\overline{\chi},\overline{\lambda},\overline{\Lambda},\overline{\Psi}'] = {} & \frac{1}{(\Phi|\hat{\overline{\mathcal{R}}}\Phi')} + (\overline{\chi}|\overline{\Psi}' - \hat{\overline{\mathcal{R}}}\Phi') \\ & + (\overline{\lambda}|\nabla_n\overline{\Psi}' - \Phi') + \langle\overline{\Lambda}|[\hat{H}-E]\overline{\Psi}'\rangle. \end{aligned} \tag{97}$$

As before, we seek such particular forms $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$ of the Lagrange functions $\overline{\chi}(\boldsymbol{\rho})$, $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$, that the first variation of the functional (97) due to small variations of its arguments $\hat{\overline{\mathcal{R}}}$, $\overline{\chi}(\boldsymbol{\rho})$, $\overline{\lambda}(\boldsymbol{\rho})$, $\overline{\Lambda}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ in the neighbourhood of $\hat{\mathcal{R}}(E)$, $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$, $\Lambda(\boldsymbol{r})$ and $\Psi'(E,\boldsymbol{r})$ vanishes. We have

$$\begin{aligned} \delta F[\Phi,\Phi';\hat{\mathcal{R}},\chi,\lambda,\Lambda,\Psi'] = {} & -\frac{(\Phi|\delta\hat{\mathcal{R}}\Phi')}{(\Phi|\hat{\mathcal{R}}\Phi')^2} + (\chi|\delta\Psi' - \delta\hat{\mathcal{R}}\Phi') \\ & + (\lambda|\nabla_n\delta\Psi') + \langle\Lambda|[\hat{H}-E]\delta\Psi'\rangle \end{aligned} \tag{98}$$

and further, after application of the Green theorem,

$$\begin{aligned} \delta F[\Phi,\Phi';\hat{\mathcal{R}},\chi,\lambda,\Lambda,\Psi'] = {} & -\left[\frac{(\Phi|\delta\hat{\mathcal{R}}\Phi')}{(\Phi|\hat{\mathcal{R}}\Phi')^2} + (\chi|\delta\hat{\mathcal{R}}\Phi')\right] + \left(\chi + \frac{\hbar^2}{2m}\nabla_n\Lambda\middle|\delta\Psi'\right) \\ & + \left(\lambda - \frac{\hbar^2}{2m}\Lambda\middle|\nabla_n\delta\Psi'\right) + \langle[\hat{H}-E]\Lambda|\delta\Psi'\rangle. \end{aligned} \tag{99}$$

On stipulating

$$\delta F[\Phi,\Phi';\hat{\mathcal{R}},\chi,\lambda,\Lambda,\Psi'] = 0 \tag{100}$$

we obtain

$$[\hat{H} - E]\Lambda(\boldsymbol{r}) = 0 \qquad \text{in } \mathcal{V} \tag{101}$$

$$\frac{1}{(\hat{\mathcal{R}}\Phi'|\Phi)^2}\Phi(\boldsymbol{\rho}) + \chi(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{102}$$

$$\chi(\boldsymbol{\rho}) + \frac{\hbar^2}{2m}\nabla_n\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{103}$$

and

$$\lambda(\boldsymbol{\rho}) - \frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{104}$$

hence

$$\chi(\boldsymbol{\rho}) = -\frac{1}{(\hat{\mathcal{R}}\Phi'|\Phi)^2}\Phi(\boldsymbol{\rho}) \tag{105}$$

and

$$\nabla_n\Lambda(\boldsymbol{\rho}) = \frac{2m}{\hbar^2}\frac{1}{(\hat{\mathcal{R}}\Phi'|\Phi)^2}\Phi(\boldsymbol{\rho}). \tag{106}$$

Before the next step, we rewrite equations (105) and (106) in more convenient forms

$$\chi(\boldsymbol{\rho}) = -\frac{1}{(\Psi'|\Phi)(\hat{\mathcal{R}}\Phi'|\Phi)}\Phi(\boldsymbol{\rho}) \tag{107}$$

and

$$\nabla_n\Lambda(\boldsymbol{\rho}) = \frac{2m}{\hbar^2}\frac{1}{(\Phi'|\Psi)(\Psi'|\Phi)}\Phi(\boldsymbol{\rho}) \tag{108}$$

where we have made use of the boundary conditions (78) and the Hermicity of the operator $\hat{\mathcal{R}}(E)$. Comparison of equations (101) and (108) with equations (1) and (77) shows that we may choose

$$\Lambda(\boldsymbol{r}) = \frac{2m}{\hbar^2}\frac{1}{(\Phi'|\Psi)(\Psi'|\Phi)}\Psi(E, \boldsymbol{r}) \tag{109}$$

and consequently

$$\lambda(\boldsymbol{\rho}) = \frac{1}{(\Phi'|\Psi)(\Psi'|\Phi)}\Psi(E, \boldsymbol{\rho}). \tag{110}$$

The dependence of the sought forms of the Lagrange functions $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$, and $\Lambda(\boldsymbol{\rho})$ on the exact solutions $\Psi(E, \boldsymbol{r})$ and $\Psi'(E, \boldsymbol{r})$ of the boundary-value problem constituted by equations (1) and (77) suggests that we may restrict ourselves to the following trial forms of the Lagrange functions

$$\overline{\chi}(\boldsymbol{\rho}) = -\frac{1}{(\overline{\Psi}'|\Phi)(\hat{\overline{\mathcal{R}}}\Phi'|\Phi)}\Phi(\boldsymbol{\rho}) \tag{111}$$

$$\overline{\lambda}(\boldsymbol{\rho}) = \frac{1}{(\Phi'|\overline{\Psi})(\overline{\Psi}'|\Phi)}\overline{\Psi}(\boldsymbol{\rho}) \tag{112}$$

and

$$\overline{\Lambda}(\boldsymbol{r}) = \frac{2m}{\hbar^2}\frac{1}{(\Phi'|\overline{\Psi})(\overline{\Psi}'|\Phi)}\overline{\Psi}(\boldsymbol{r}). \tag{113}$$

Substitution of these particular forms of $\overline{\chi}(\boldsymbol{\rho})$, $\overline{\lambda}(\boldsymbol{\rho})$ and $\overline{\Lambda}(\boldsymbol{r})$ to the definition (79) gives a fractional functional

$$F[\Phi, \Phi'; \overline{\Psi}, \overline{\Psi}'] = \frac{(\overline{\Psi}|\nabla_n\overline{\Psi}')}{(\Phi|\overline{\Psi}')(\overline{\Psi}|\Phi')} + \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle}{(\Phi|\overline{\Psi}')(\overline{\Psi}|\Phi')} \tag{114}$$

possessing the symmetry property (95). The sought variational principle is

$$(\Phi|\hat{\mathcal{R}}\Phi')^{-1} = \text{stat}\left\{\frac{(\overline{\Psi}|\nabla_n\overline{\Psi}')}{(\Phi|\overline{\Psi}')(\overline{\Psi}|\Phi')} + \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle}{(\Phi|\overline{\Psi}')(\overline{\Psi}|\Phi')}\right\} \tag{115}$$

hence, it also follows that

$$(\Phi|\hat{\mathcal{R}}\Phi') = \text{stat}\left\{\frac{(\Phi|\overline{\Psi}')(\overline{\Psi}|\Phi')}{(\overline{\Psi}|\nabla_n\overline{\Psi}') + (2m/\hbar^2)\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle}\right\}. \tag{116}$$

Equations (115) and (116) are independent of the normalization of the trial functions $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$. A particular form of the variational principle (115) with $\Phi(\boldsymbol{\rho}) = \Phi'(\boldsymbol{\rho})$ and $\overline{\Psi}(\boldsymbol{r}) = \overline{\Psi}'(\boldsymbol{r})$ was considered by Nesbet [19, 20].

3.4. The variational principles for matrix elements of $\hat{\mathcal{B}}(E)$ and their reciprocals

Finally, we may construct variational principles for a matrix element $(\Phi|\hat{\mathcal{B}}\Phi')$ and its inverse, $(\Phi|\hat{\mathcal{B}}\Phi')^{-1}$, where $\hat{\mathcal{B}}(E)$ is the integral operator defined in section 2 while $\Phi(\boldsymbol{\rho})$ and $\Phi'(\boldsymbol{\rho})$ are any two reasonable functions defined on the surface $\mathcal{S}$. For this purpose, we introduce two functions $\Psi(E, \boldsymbol{r})$ and $\Psi'(E, \boldsymbol{r})$ belonging to $\mathcal{D}(E)$ and satisfying on the surface $\mathcal{S}$ *inhomogeneous Dirichlet* boundary conditions

$$\Psi(E, \boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \qquad \Psi'(E, \boldsymbol{\rho}) = \Phi'(\boldsymbol{\rho}). \tag{117}$$

Acting on both sides of equations (117) with the operator $\hat{\mathcal{B}}(E)$ and utilizing equation (8) we may rewrite these boundary conditions in the form

$$\nabla_n\Psi(E, \boldsymbol{\rho}) = \hat{\mathcal{B}}(E)\Phi(\boldsymbol{\rho}) \qquad \nabla_n\Psi'(E, \boldsymbol{\rho}) = \hat{\mathcal{B}}(E)\Phi'(\boldsymbol{\rho}). \tag{118}$$

To derive the variational principle for $(\Phi|\hat{\mathcal{B}}\Phi')$, we treat equations (1), (117) and (118) as constraints and consider a functional

$$F[\Phi, \Phi'; \hat{\overline{\mathcal{B}}}, \overline{\chi}, \overline{\lambda}, \overline{\Lambda}, \overline{\Psi}'] = (\Phi|\hat{\overline{\mathcal{B}}}\Phi') + (\overline{\chi}|\nabla_n\overline{\Psi}' - \hat{\overline{\mathcal{B}}}\Phi') + (\overline{\lambda}|\overline{\Psi}' - \Phi') + \langle\overline{\Lambda}|[\hat{H}-E]\overline{\Psi}'\rangle. \tag{119}$$

Here $\hat{\overline{\mathcal{B}}}$ is a linear integral operator, possibly non-Hermitean, acting on functions defined on the surface $\mathcal{S}$, $\overline{\chi}(\boldsymbol{\rho})$ and $\overline{\lambda}(\boldsymbol{\rho})$ belong to a class of well behaving functions defined on $\mathcal{S}$ while $\overline{\Lambda}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ are some reasonable functions defined in the volume $\mathcal{V}$. The first variation of the functional (119) due to variations of $\hat{\overline{\mathcal{B}}}$, $\overline{\chi}(\boldsymbol{\rho})$, $\overline{\lambda}(\boldsymbol{\rho})$, $\overline{\Lambda}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ around $\hat{\mathcal{B}}(E)$, $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$, $\Lambda(\boldsymbol{r})$ and $\Psi'(E, \boldsymbol{r})$, respectively, is

$$\delta F[\Phi, \Phi'; \hat{\mathcal{B}}, \chi, \lambda, \Lambda, \Psi'] = (\Phi|\delta\hat{\mathcal{B}}\Phi') + (\chi|\nabla_n\delta\Psi - \delta\hat{\mathcal{B}}\Phi') + (\lambda|\delta\Psi') + \langle\Lambda|[\hat{H}-E]\delta\Psi'\rangle \tag{120}$$

and, after application of the Green theorem to the volume integral, may be rewritten as

$$\begin{aligned}\delta F[\Phi, \Phi'; \hat{\mathcal{B}}, \chi, \lambda, \Lambda, \Psi'] = {} & (\Phi - \chi|\delta\hat{\mathcal{B}}\Phi') + \left(\lambda + \frac{\hbar^2}{2m}\nabla_n\Lambda\middle|\,\delta\Psi'\right) \\ & + \left(\chi - \frac{\hbar^2}{2m}\Lambda\middle|\,\nabla_n\delta\Psi'\right) + \langle[\hat{H}-E]\Lambda|\delta\Psi'\rangle.\end{aligned} \tag{121}$$

On stipulating

$$\delta F[\Phi, \Phi'; \hat{\mathcal{B}}, \chi, \lambda, \Lambda, \Psi'] = 0 \tag{122}$$

we obtain a set of conditions which must be satisfied by the sought functions $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$

$$[\hat{H} - E]\Lambda(\boldsymbol{r}) = 0 \qquad \text{in } \mathcal{V} \tag{123}$$

$$\Phi(\boldsymbol{\rho}) - \chi(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{124}$$

$$\lambda(\boldsymbol{\rho}) + \frac{\hbar^2}{2m}\nabla_n \Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{125}$$

and

$$\chi(\boldsymbol{\rho}) - \frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{126}$$

hence, it follows that

$$\chi(\boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \tag{127}$$

and

$$\Lambda(\boldsymbol{\rho}) = \frac{2m}{\hbar^2}\Phi(\boldsymbol{\rho}). \tag{128}$$

Comparison of equations (123) and (128) with equations (1) and (117) shows that we may choose

$$\Lambda(\boldsymbol{r}) = \frac{2m}{\hbar^2}\Psi(E, \boldsymbol{r}) \tag{129}$$

and consequently

$$\lambda(\boldsymbol{\rho}) = -\nabla_n \Psi(E, \boldsymbol{\rho}). \tag{130}$$

The expressions (130), (127) and (129) for the Lagrange functions $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$ suggest the following natural choices of their trial forms

$$\overline{\chi}(\boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \tag{131}$$

$$\overline{\lambda}(\boldsymbol{\rho}) = -\nabla_n \overline{\Psi}(\boldsymbol{\rho}) \tag{132}$$

and

$$\overline{\Lambda}(\boldsymbol{r}) = \frac{2m}{\hbar^2}\overline{\Psi}(\boldsymbol{r}) \tag{133}$$

yielding the functional

$$F[\Phi, \Phi'; \overline{\Psi}, \overline{\Psi}'] = (\Phi|\nabla_n \overline{\Psi}') + (\nabla_n \overline{\Psi}|\Phi') - (\nabla_n \overline{\Psi}|\overline{\Psi}') + \frac{2m}{\hbar^2}\langle \overline{\Psi}|[\hat{H} - E]\overline{\Psi}'\rangle. \tag{134}$$

On applying the Green integration formula to the volume integral on the right-hand side of this equation, one easily shows that the functional (134) satisfies the symmetry relation (95). Concluding, we have the variational principle

$$(\Phi|\hat{\mathcal{B}}\Phi') = \text{stat}\left\{(\Phi|\nabla_n \overline{\Psi}') + (\nabla_n \overline{\Psi}|\Phi') - (\nabla_n \overline{\Psi}|\overline{\Psi}') + \frac{2m}{\hbar^2}\langle \overline{\Psi}|[\hat{H} - E]\overline{\Psi}'\rangle\right\}. \tag{135}$$

It remains to construct the variational principle for $(\Phi|\hat{\mathcal{B}}\Phi')^{-1}$. We treat equations (1), (117) and (118) as constraints and consider the functional

$$F[\Phi, \Phi'; \hat{\overline{\mathcal{B}}}, \overline{\chi}, \overline{\lambda}, \overline{\Lambda}, \overline{\Psi}'] = \frac{1}{(\Phi|\hat{\overline{\mathcal{B}}}\Phi')} + (\overline{\chi}|\nabla_n \overline{\Psi}' - \hat{\overline{\mathcal{B}}}\Phi') + (\overline{\lambda}|\overline{\Psi}' - \Phi') + \langle \overline{\Lambda}|[\hat{H} - E]\overline{\Psi}'\rangle. \tag{136}$$

Its first variation due to variations of its arguments around their sought forms

$$\delta F[\Phi, \Phi'; \hat{\mathcal{B}}, \chi, \lambda, \Lambda, \Psi'] = -\frac{(\Phi|\delta\hat{\mathcal{B}}\Phi')}{(\Phi|\hat{\mathcal{B}}\Phi')^2} + (\chi|\nabla_n\delta\Psi' - \delta\hat{\mathcal{B}}\Phi') + (\lambda|\delta\Psi') + \langle\Lambda|[\hat{H} - E]\delta\Psi'\rangle \tag{137}$$

may be rewritten, on transforming the volume integral, in the form

$$\delta F[\Phi, \Phi'; \hat{\mathcal{B}}, \chi, \lambda, \Lambda, \Psi'] = -\left[\frac{(\Phi|\delta\hat{\mathcal{B}}\Phi')}{(\Phi|\hat{\mathcal{B}}\Phi')^2} + (\chi|\delta\hat{\mathcal{B}}\Phi')\right] + \left(\lambda + \frac{\hbar^2}{2m}\nabla_n\Lambda\middle|\delta\Psi'\right) + \left(\chi - \frac{\hbar^2}{2m}\Lambda\middle|\nabla_n\delta\Psi'\right) + \langle[\hat{H} - E]\Lambda|\delta\Psi'\rangle. \tag{138}$$

On attempting to have the variational principle, we stipulate

$$\delta F[\Phi, \Phi'; \hat{\mathcal{B}}, \chi, \lambda, \Lambda, \Psi'] = 0 \tag{139}$$

obtaining the conditions

$$[\hat{H} - E]\Lambda(\boldsymbol{r}) = 0 \qquad \text{in } \mathcal{V} \tag{140}$$

$$\frac{1}{(\hat{\mathcal{B}}\Phi'|\Phi)^2}\Phi(\boldsymbol{\rho}) + \chi(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{141}$$

$$\lambda(\boldsymbol{\rho}) + \frac{\hbar^2}{2m}\nabla_n\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{142}$$

and

$$\chi(\boldsymbol{\rho}) - \frac{\hbar^2}{2m}\Lambda(\boldsymbol{\rho}) = 0 \qquad \text{on } \mathcal{S} \tag{143}$$

hence

$$\chi(\boldsymbol{\rho}) = -\frac{1}{(\hat{\mathcal{B}}\Phi'|\Phi)^2}\Phi(\boldsymbol{\rho}) \tag{144}$$

and

$$\Lambda(\boldsymbol{\rho}) = -\frac{2m}{\hbar^2}\frac{1}{(\hat{\mathcal{B}}\Phi'|\Phi)^2}\Phi(\boldsymbol{\rho}). \tag{145}$$

Utilizing the boundary conditions (118) and the Hermicity of the operator $\hat{\mathcal{B}}(E)$, it is convenient to rewrite equations (144) and (145) in the forms

$$\chi(\boldsymbol{\rho}) = -\frac{1}{(\nabla_n\Psi'|\Phi)(\hat{\mathcal{B}}\Phi'|\Phi)}\Phi(\boldsymbol{\rho}) \tag{146}$$

and

$$\Lambda(\boldsymbol{\rho}) = -\frac{2m}{\hbar^2}\frac{1}{(\Phi'|\nabla_n\Psi)(\nabla_n\Psi'|\Phi)}\Phi(\boldsymbol{\rho}). \tag{147}$$

On comparing equations (140) and (147) with equations (1) and (117) we find that the function $\Lambda(\boldsymbol{r})$ may be chosen in the form

$$\Lambda(\boldsymbol{r}) = -\frac{2m}{\hbar^2}\frac{1}{(\Phi'|\nabla_n\Psi)(\nabla_n\Psi'|\Phi)}\Psi(E, \boldsymbol{r}) \tag{148}$$

and consequently (cf equation (142))

$$\lambda(\boldsymbol{\rho}) = \frac{1}{(\Phi'|\nabla_n\Psi)(\nabla_n\Psi'|\Phi)}\nabla_n\Psi(E, \boldsymbol{\rho}). \tag{149}$$

This suggests the following optimal choices of the trial forms of the Lagrange functions $\chi(\boldsymbol{\rho})$, $\lambda(\boldsymbol{\rho})$ and $\Lambda(\boldsymbol{r})$

$$\overline{\chi}(\boldsymbol{\rho}) = -\frac{1}{(\nabla_n\overline{\Psi}'|\Phi)(\hat{\overline{\mathcal{B}}}\Phi'|\Phi)}\Phi(\boldsymbol{\rho}) \tag{150}$$

$$\overline{\lambda}(\boldsymbol{\rho}) = \frac{1}{(\Phi'|\nabla_n\overline{\Psi})(\nabla_n\overline{\Psi}'|\Phi)}\nabla_n\overline{\Psi}(\boldsymbol{\rho}) \tag{151}$$

and

$$\overline{\Lambda}(\boldsymbol{r}) = -\frac{2m}{\hbar^2}\frac{1}{(\Phi'|\nabla_n\overline{\Psi})(\nabla_n\overline{\Psi}'|\Phi)}\overline{\Psi}(\boldsymbol{r}) \tag{152}$$

leading to a symmetric (in the sense of equation (95)) fractional functional

$$F[\Phi, \Phi'; \overline{\Psi}, \overline{\Psi}'] = \frac{(\nabla_n\overline{\Psi}|\overline{\Psi}')}{(\Phi|\nabla_n\overline{\Psi}')(\nabla_n\overline{\Psi}|\Phi')} - \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle}{(\Phi|\nabla_n\overline{\Psi}')(\nabla_n\overline{\Psi}|\Phi')}. \tag{153}$$

Thus, the desired variational principle for $(\Phi|\hat{\mathcal{B}}\Phi')^{-1}$ is

$$(\Phi|\hat{\mathcal{B}}\Phi')^{-1} = \text{stat}\left\{\frac{(\nabla_n\overline{\Psi}|\overline{\Psi}')}{(\Phi|\nabla_n\overline{\Psi}')(\nabla_n\overline{\Psi}|\Phi')} - \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle}{(\Phi|\nabla_n\overline{\Psi}')(\nabla_n\overline{\Psi}|\Phi')}\right\}. \tag{154}$$

From equation (154) it also follows that

$$(\Phi|\hat{\mathcal{B}}\Phi') = \text{stat}\left\{\frac{(\Phi|\nabla_n\overline{\Psi}')(\nabla_n\overline{\Psi}|\Phi')}{(\nabla_n\overline{\Psi}|\overline{\Psi}') - (2m/\hbar^2)\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle}\right\}. \tag{155}$$

This result is obtained in a different way by Nesbet [20]. The variational principle (155) has the advantage over (135) in being independent of the normalization of the trial functions $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$.

4. Variational principles with constrained trial functions

In the course of the derivation of the variational principles presented in section 3, we have not imposed any constraints on trial functions apart from a tacit reasonable assumption that the functions and their first derivatives are continuous across any surface dividing the volume $\mathcal{V}$ into smaller subregions. It is interesting to investigate how the variational principles derived above are influenced if we impose some *additional* constraints on trial functions used. At first, let us consider the variational principle for the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')$ discussed in section 3.3. There we have shown that the functional

$$F[\Phi, \Phi'; \overline{\Psi}, \overline{\Psi}'] = (\Phi|\overline{\Psi}') + (\overline{\Psi}|\Phi') - (\overline{\Psi}|\nabla_n\overline{\Psi}') - \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}'\rangle \tag{156}$$

is stationary with respect to small and otherwise arbitrary variations of the trial functions $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ around $\Psi(E, \boldsymbol{r})$ and $\Psi'(E, \boldsymbol{r})$, respectively, where the latter functions are defined as those particular solutions of the Schrödinger equation (1) in the volume $\mathcal{V}$ that on the enclosing surface $\mathcal{S}$ satisfy the inhomogeneous Neumann boundary conditions

$$\nabla_n\Psi(E, \boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \qquad \nabla_n\Psi'(E, \boldsymbol{\rho}) = \Phi'(\boldsymbol{\rho}). \tag{157}$$

The stationary value of the functional (156) is the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')$. We emphasize that, in the general case discussed in section 3.3, the trial functions $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ are *not* constrained to satisfy the same boundary conditions on the surface $\mathcal{S}$ as the exact functions $\Psi(E, \boldsymbol{r})$ and $\Psi'(E, \boldsymbol{r})$ do. Let us, however, restrict our considerations to a class of those

trial functions $\overline{\Psi}(\boldsymbol{r})$ and $\overline{\Psi}'(\boldsymbol{r})$ that on the surface $\mathcal{S}$ do satisfy the boundary conditions (157), i.e. those that

$$\nabla_n\overline{\Psi}(\boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \qquad \nabla_n\overline{\Psi}'(\boldsymbol{\rho}) = \Phi'(\boldsymbol{\rho}). \tag{158}$$

Then the second and third terms on the right-hand side of equation (156) cancel and the functional becomes

$$F[\Phi, \Phi'; \overline{\Psi}, \overline{\Psi}'] = (\Phi|\overline{\Psi}') - \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{H} - E]\overline{\Psi}'\rangle \tag{159}$$

hence, we obtain the Jackson variational principle [12]

$$(\Phi|\hat{\mathcal{R}}\Phi') = \text{stat}\left\{(\Phi|\overline{\Psi}') - \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{H} - E]\overline{\Psi}'\rangle\right\} \tag{160}$$

where the trial functions are constrained to satisfy the boundary conditions (158).

Similar considerations may be carried out in the case of the variational principle for the matrix element $(\Phi|\hat{\mathcal{B}}\Phi')$ derived in section 3.4. If in the variational principle (135) we restrict a class of admissible trial functions to those that on the surface $\mathcal{S}$ satisfy the inhomogeneous Dirichlet boundary conditions

$$\overline{\Psi}(\boldsymbol{\rho}) = \Phi(\boldsymbol{\rho}) \qquad \overline{\Psi}'(\boldsymbol{\rho}) = \Phi'(\boldsymbol{\rho}) \tag{161}$$

we obtain the analogy of the Jackson variational principle [45, 47]

$$(\Phi|\hat{\mathcal{B}}\Phi') = \text{stat}\left\{(\Phi|\nabla_n\overline{\Psi}') + \frac{2m}{\hbar^2}\langle\overline{\Psi}|[\hat{H} - E]\overline{\Psi}'\rangle\right\}. \tag{162}$$

In the similar way one may obtain restricted variational principles for $(\Phi|\hat{\mathcal{R}}\Phi')^{-1}$ and $(\Phi|\hat{\mathcal{B}}\Phi')^{-1}$.

5. Use of the Rayleigh–Ritz trial functions

Variational principles derived in sections 3 and 4 provide a convenient way of finding approximate values of the matrix elements and eigenvalues of the operators $\hat{\mathcal{R}}(E)$ and $\hat{\mathcal{B}}(E)$. One may use a class of trial functions depending on some parameters and optimize values of the latter by requiring that a relevant functional be stationary with respect to small variations of the parameters. Subsequent substitution of the optimal (within the class admitted) trial functions determined in this way into the functional gives a variational estimate of the quantity considered.

Particularly useful in applications are the Rayleigh–Ritz trial functions of the form

$$\overline{\Psi}(\boldsymbol{r}) = \sum_i c_i\phi_i(\boldsymbol{r}) \tag{163}$$

where the coordinate functions $\{\phi_i(\boldsymbol{r})\}$ are chosen from a complete set $\mathcal{X}$ of functions spanning the interior of the volume $\mathcal{V}$ *and* the surface $\mathcal{S}$. The coefficients $\{c_i\}$ are variational parameters and must be determined. In the following subsections we shall use the Rayleigh–Ritz trial functions to find variational estimates of matrix elements and eigenvalues of the operators $\hat{\mathcal{R}}(E)$ and $\hat{\mathcal{B}}(E)$.

5.1. The variational principle for matrix elements of $\hat{\mathcal{R}}(E)$

As the first example, we shall use the Rayleigh–Ritz trial functions

$$\overline{\Psi}(\boldsymbol{r}) = \sum_{i=1}^{N} c_i \phi_i(\boldsymbol{r}) \qquad \overline{\Psi}'(\boldsymbol{r}) = \sum_{i=1}^{N} c_i' \phi_i(\boldsymbol{r}) \tag{164}$$

in the variational principle (96) for the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')$. In equation (164) N is a number (the same in both expansions) of coordinate functions used. Substitution of these particular forms of the trial functions into functional (94) gives

$$F[\Phi, \Phi'; \{c_i^*\}, \{c_i'\}] = \sum_{i=1}^{N} c_i'(\Phi|\phi_i) + \sum_{i=1}^{N} c_i^*(\phi_i|\Phi') - \sum_{i,j=1}^{N} c_i^* c_j'(\phi_i|\nabla_n \phi_j) - \frac{2m}{\hbar^2} \sum_{i,j=1}^{N} c_i^* c_j' \langle \phi_i|[\hat{H} - E]\phi_j\rangle. \tag{165}$$

Using a more convenient matrix notation we rewrite equation (165) in a compact form

$$F[\boldsymbol{f}^\dagger, \boldsymbol{f}'; \boldsymbol{c}^\dagger, \boldsymbol{c}'] = \boldsymbol{f}^\dagger \boldsymbol{c}' + \boldsymbol{c}^\dagger \boldsymbol{f}' - \boldsymbol{c}^\dagger \mathbf{S} \boldsymbol{c}' \tag{166}$$

where $\boldsymbol{f}^\dagger$ and $\boldsymbol{c}^\dagger$ are N-dimensional *row* vectors with elements $\{f_i^* = (\Phi|\phi_i)\}$ and $\{c_i^*\}$, respectively, $\boldsymbol{f}'$ and $\boldsymbol{c}'$ are N-dimensional *column* vectors with elements $\{f_i' = (\phi_i|\Phi')\}$ and $\{c_i'\}$, respectively, and $\mathbf{S}$ is a Hermitean $N \times N$ matrix with elements

$$S_{ij} = (\phi_i|\nabla_n \phi_j) + \frac{2m}{\hbar^2} \langle \phi_i|[\hat{H} - E]\phi_j\rangle. \tag{167}$$

The first variation of the functional (165) due to small variations of the vectors $\boldsymbol{c}^\dagger$ and $\boldsymbol{c}'$ is

$$\delta F[\boldsymbol{f}^\dagger, \boldsymbol{f}'; \boldsymbol{c}^\dagger, \boldsymbol{c}'] = [\boldsymbol{f}^\dagger - \boldsymbol{c}^\dagger \mathbf{S}]\delta \boldsymbol{c}' + \delta \boldsymbol{c}^\dagger [\boldsymbol{f}' - \mathbf{S}\boldsymbol{c}']. \tag{168}$$

On stipulating

$$\delta F[\boldsymbol{f}^\dagger, \boldsymbol{f}'; \boldsymbol{c}^\dagger, \boldsymbol{c}'] = 0 \tag{169}$$

we obtain

$$\boldsymbol{f}^\dagger - \boldsymbol{c}^\dagger \mathbf{S} = 0 \qquad \boldsymbol{f}' - \mathbf{S}\boldsymbol{c}' = 0 \tag{170}$$

hence

$$\boldsymbol{c}^\dagger = \boldsymbol{f}^\dagger \mathbf{S}^{-1} \qquad \boldsymbol{c}' = \mathbf{S}^{-1} \boldsymbol{f}'. \tag{171}$$

Substitution of these optimal forms of the vectors $\boldsymbol{c}^\dagger$ and $\boldsymbol{c}'$ into equation (166) yields a variational estimate of the matrix element $(\Phi|\hat{\mathcal{R}}\Phi')$ (cf also [27, 19, 20])

$$(\Phi|\hat{\tilde{\mathcal{R}}}\Phi') = \boldsymbol{f}^\dagger \mathbf{S}^{-1} \boldsymbol{f}' \equiv \sum_{i,j=1}^{N} (\Phi|\phi_i)(\mathbf{S}^{-1})_{ij}(\phi_j|\Phi'). \tag{172}$$

Since the functions $\Phi(\boldsymbol{\rho})$ and $\Phi'(\boldsymbol{\rho})$ are arbitrary, from equation (172) we obtain a variational estimate of the kernel $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ (cf also [20])

$$\tilde{\mathcal{R}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{i,j=1}^{N} \phi_i(\boldsymbol{\rho})(\mathbf{S}^{-1})_{ij} \phi_j^*(\boldsymbol{\rho}') \tag{173}$$

which is manifestly Hermitean.

It is interesting that $(\Phi|\hat{\tilde{\mathcal{R}}}\Phi')$ and $\tilde{\mathcal{R}}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$ may be conveniently written as ratios of two determinants†. On utilizing equation (213) derived in the appendix, we find from equations (172) and (173)

$$(\Phi|\hat{\tilde{\mathcal{R}}}\Phi') = -\frac{\det\begin{pmatrix}\mathbf{S} & \boldsymbol{f}' \\ \boldsymbol{f}^\dagger & 0\end{pmatrix}}{\det\mathbf{S}} \tag{174}$$

and

$$\tilde{\mathcal{R}}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = -\frac{\det\begin{pmatrix}\mathbf{S} & \boldsymbol{\phi}^\dagger(\boldsymbol{\rho}') \\ \boldsymbol{\phi}(\boldsymbol{\rho}) & 0\end{pmatrix}}{\det\mathbf{S}} \tag{175}$$

where $\boldsymbol{\phi}(\boldsymbol{\rho})$ is an N-dimensional *row* vector with elements $\{\phi_i(\boldsymbol{\rho})\}$ and $\boldsymbol{\phi}^\dagger(\boldsymbol{\rho}')$ is an N-dimensional *column* vector with elements $\{\phi_i^*(\boldsymbol{\rho}')\}$.

If in the expansions (164) *all* basis functions from the complete set $\mathcal{X}$ are included, we have an *exact* expansion of the kernel $\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$

$$\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_{\text{all } i,\,j}\phi_i(\boldsymbol{\rho})(\mathbf{S}^{-1})_{ij}\phi_j^*(\boldsymbol{\rho}'). \tag{176}$$

Equations (172) and (173) may be derived in an alternative way if, instead of the variational principle (96), one uses the variational principle (116). This agrees with results obtained by Nesbet [19, 20]. We leave the derivation as an exercise to the reader.

5.2. The variational principle for matrix elements of $\hat{\mathcal{B}}(E)$

Similar considerations lead us to a variational estimate of the kernel $\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$. Substitution of the trial functions of the form (164) to the functional (134) gives

$$F[\boldsymbol{g}^\dagger,\boldsymbol{g}';\boldsymbol{c}^\dagger,\boldsymbol{c}'] = \boldsymbol{g}^\dagger\boldsymbol{c}' + \boldsymbol{c}^\dagger\boldsymbol{g}' - \boldsymbol{c}^\dagger\mathbf{T}\boldsymbol{c}' \tag{177}$$

where $\boldsymbol{g}^\dagger$ is an N-dimensional *row* vector with elements $\{g_i^* = (\Phi|\nabla_n\phi_i)\}$, $\boldsymbol{g}'$ is an N-dimensional *column* vector with elements $\{g_i' = (\nabla_n\phi_i|\Phi')\}$ and $\mathbf{T}$ is a Hermitean $N\times N$ matrix with elements

$$T_{ij} = (\nabla_n\phi_i|\phi_j) - \frac{2m}{\hbar^2}\langle\phi_i|[\hat{H}-E]\phi_j\rangle. \tag{178}$$

Stipulation

$$\delta F[\boldsymbol{g}^\dagger,\boldsymbol{g}';\boldsymbol{c}^\dagger,\boldsymbol{c}'] = 0 \tag{179}$$

yields the following optimal forms of the vectors of the expansion coefficients

$$\boldsymbol{c}^\dagger = \boldsymbol{g}^\dagger\mathbf{T}^{-1} \qquad \boldsymbol{c}' = \mathbf{T}^{-1}\boldsymbol{g}' \tag{180}$$

hence, we obtain variational estimates of the matrix element $(\Phi|\hat{\mathcal{B}}\Phi')$

$$(\Phi|\hat{\tilde{\mathcal{B}}}\Phi') = \boldsymbol{g}^\dagger\mathbf{T}^{-1}\boldsymbol{g}' \equiv \sum_{i,j=1}^{N}(\Phi|\nabla_n\phi_i)(\mathbf{T}^{-1})_{ij}(\nabla_n\phi_j|\Phi') \tag{181}$$

and of the kernel $\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}')$

$$\tilde{\mathcal{B}}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_{i,j=1}^{N}\nabla_n\phi_i(\boldsymbol{\rho})(\mathbf{T}^{-1})_{ij}\nabla_n\phi_j^*(\boldsymbol{\rho}'). \tag{182}$$

† Other determinantal expressions related to the R-matrix theory are discussed in [53].

It should be noticed that the kernel $\tilde{\mathcal{B}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ obtained in this way is automatically Hermitean.

Similar to the case discussed in the preceding subsection, $(\Phi|\hat{\tilde{\mathcal{B}}}\Phi')$ and $\tilde{\mathcal{B}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ may be conveniently expressed as ratios of determinants. Utilizing equations (213), (181) and (182) we find

$$(\Phi|\hat{\tilde{\mathcal{B}}}\Phi') = -\frac{\det\begin{pmatrix} \mathbf{T} & \boldsymbol{g}' \\ \boldsymbol{g}^\dagger & 0 \end{pmatrix}}{\det \mathbf{T}} \tag{183}$$

and

$$\tilde{\mathcal{B}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = -\frac{\det\begin{pmatrix} \mathbf{T} & \nabla_n\phi^\dagger(\boldsymbol{\rho}') \\ \nabla_n\phi(\boldsymbol{\rho}) & 0 \end{pmatrix}}{\det \mathbf{T}} \tag{184}$$

where $\nabla_n\phi(\boldsymbol{\rho})$ is an N-dimensional *row* vector with elements $\{\nabla_n\phi_i(\boldsymbol{\rho})\}$ and $\nabla_n\phi^\dagger(\boldsymbol{\rho}')$ is an N-dimensional *column* vector with elements $\{\nabla_n\phi_i^*(\boldsymbol{\rho}')\}$.

If all functions from the basis set $\mathcal{X}$ are included in the expansion (164), we have an exact expansion of the kernel $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$

$$\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{\text{all } i,\, j} \nabla_n\phi_i(\boldsymbol{\rho})(\mathbf{T}^{-1})_{ij}\nabla_n\phi_j^*(\boldsymbol{\rho}'). \tag{185}$$

A derivation of equations (181) and (182) from the variational principle (155) is left to the reader as an exercise.

5.3. The variational principle for eigenvalues of $\hat{\mathcal{B}}(E)$

The Rayleigh–Ritz trial functions may also be used [28, 40] in the variational principle for eigenvalues of the operator $\hat{\mathcal{B}}(E)$ derived in section 3.1. To illustrate this, we seek approximate eigenfunctions of $\hat{\mathcal{B}}(E)$ in the form

$$\overline{\Psi}(\boldsymbol{r}) = \sum_{i=1}^{N} c_i\phi_i(\boldsymbol{r}). \tag{186}$$

Substitution of this trial function to the functional (49) gives

$$F[\boldsymbol{c}^\dagger, \boldsymbol{c}] = \frac{\boldsymbol{c}^\dagger\mathbf{S}\boldsymbol{c}}{\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c}} \tag{187}$$

where the vectors $\boldsymbol{c}^\dagger$ and $\boldsymbol{c}$ are defined as in section 5.1, elements of the Hermitean matrix $\mathbf{S}$ are defined as in equation (167) and $\mathbf{M}$ is a Hermitean $N \times N$ 'surface' overlap matrix with elements

$$M_{ij} = (\phi_i|\phi_j). \tag{188}$$

The first variation of the functional (187) due to small variations of the vectors $\boldsymbol{c}^\dagger$ and $\boldsymbol{c}$ is

$$\delta F[\boldsymbol{c}^\dagger, \boldsymbol{c}] = \frac{\delta\boldsymbol{c}^\dagger\left[(\mathbf{S}\boldsymbol{c})(\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c}) - (\mathbf{M}\boldsymbol{c})(\boldsymbol{c}^\dagger\mathbf{S}\boldsymbol{c})\right]}{(\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c})^2} + \frac{\left[(\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c})(\boldsymbol{c}^\dagger\mathbf{S}) - (\boldsymbol{c}^\dagger\mathbf{S}\boldsymbol{c})(\boldsymbol{c}^\dagger\mathbf{M})\right]\delta\boldsymbol{c}}{(\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c})^2}. \tag{189}$$

To find optimal expansion coefficients $\{c_i\}$ we require

$$\delta F[\boldsymbol{c}^\dagger, \boldsymbol{c}] = 0 \tag{190}$$

which results in matrix equations

$$\mathbf{S}\boldsymbol{c} = \frac{\boldsymbol{c}^\dagger\mathbf{S}\boldsymbol{c}}{\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c}}\mathbf{M}\boldsymbol{c} \qquad \boldsymbol{c}^\dagger\mathbf{S} = \frac{\boldsymbol{c}^\dagger\mathbf{S}\boldsymbol{c}}{\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c}}\boldsymbol{c}^\dagger\mathbf{M}. \tag{191}$$

Denoting

$$\tilde{b} = \frac{\boldsymbol{c}^\dagger\mathbf{S}\boldsymbol{c}}{\boldsymbol{c}^\dagger\mathbf{M}\boldsymbol{c}} \tag{192}$$

we find that $\tilde{b}$ is an eigenvalue while $\boldsymbol{c}$ and $\boldsymbol{c}^\dagger$ are the corresponding right and left eigenvectors of generalized matrix eigenvalue problems

$$\mathbf{S}\boldsymbol{c} = \tilde{b}\mathbf{M}\boldsymbol{c} \qquad \boldsymbol{c}^\dagger\mathbf{S} = \tilde{b}\boldsymbol{c}^\dagger\mathbf{M}. \tag{193}$$

The eigenvalue equations (193) must be handled with care since, in general, the rank of the matrix $\mathbf{M}$ will be far smaller than the number N of coordinate functions $\{\phi_i(\boldsymbol{r})\}$ included in equation (186). This happens because a number of functions that are linearly independent on the surface $\mathcal{S}$ is smaller than the number of functions spanning simultaneously the surface $\mathcal{S}$ *and* the volume $\mathcal{V}$†. Therefore, it is very likely that the coordinate functions chosen will be linearly dependent *on the surface* $\mathcal{S}$ and the determinant of the matrix $\mathbf{M}$ (a Gram determinant for the N surface functions $\{\phi_i(\boldsymbol{\rho})\}$) will vanish. In fact, this *should* be so if our approximation of the function $\Psi(E, \boldsymbol{r})$ is to be equally good on the surface $\mathcal{S}$ and in the interior of the volume $\mathcal{V}$.

Effective algorithms for solving singular eigenvalue problems of the form (193) were worked out [54, 55] and computer codes based on Moler and Stewart's algorithm [55] are available (for instance [56], see also [32] cited in [28]). Once all eigenvalues $\{\tilde{b}_k\}$ and the corresponding right eigenvectors $\{\boldsymbol{c}_k\}$ for the eigenproblem (193) have been found, one may obtain estimates of the kernels $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ and $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$. In analogy with the spectral expansions (25) and (27) we have

$$\tilde{\mathcal{B}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{k=1}^{\text{rank }\mathbf{M}} \overline{\Psi}_k(\boldsymbol{\rho})\tilde{b}_k\overline{\Psi}_k^*(\boldsymbol{\rho}') = \sum_{i,j=1}^{N} \phi_i(\boldsymbol{\rho})\left[\sum_{k=1}^{\text{rank }\mathbf{M}} c_{ik}\tilde{b}_k c_{jk}^*\right]\phi_j^*(\boldsymbol{\rho}') \tag{194}$$

(c_{ik} is an ith element of the eigenvector $\boldsymbol{c}_k$) and

$$\tilde{\mathcal{R}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{k=1}^{\text{rank }\mathbf{M}} \overline{\Psi}_k(\boldsymbol{\rho})\tilde{b}_k^{-1}\overline{\Psi}_k^*(\boldsymbol{\rho}') = \sum_{i,j=1}^{N} \phi_i(\boldsymbol{\rho})\left[\sum_{k=1}^{\text{rank }\mathbf{M}} c_{ik}\tilde{b}_k^{-1} c_{jk}^*\right]\phi_j^*(\boldsymbol{\rho}'). \tag{195}$$

It must be emphasized that the estimates (194) and (195) of the kernels $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ and $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ are *not* variational estimates. Although the approximations $\{\tilde{b}_k\}$ of the eigenvalues of the operator $\hat{\mathcal{B}}(E)$ obtained by solving the matrix eigenvalue problem (193) are correct to second order, the coefficients $\{c_{ik}\}$ extracted from the eigenvectors $\{\boldsymbol{c}_k\}$, and consequently our optimal approximations $\{\overline{\Psi}_k(\boldsymbol{\rho})\}$ of the surface eigenfunctions $\{\Psi_k(E, \boldsymbol{\rho})\}$, are good, by definition, only to first order. Therefore, the kernels $\tilde{\mathcal{B}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}', E)$ and $\tilde{\mathcal{R}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}', E)$ given by equations (194) and (195) will also have first-order errors. This deficiency of methods based on variational determination of eigenvalues was already pointed out by Kohn [11] in the context of the S-matrix theory.

† This is particularly well visible in one-dimensional R-matrix problems when the volume $\mathcal{V}$ is an interval. A number of functions that are linearly independent on the surface $\mathcal{S}$ (two ends of the interval) is two but one needs an infinite number of basis functions to span the interior of the interval and the ends.

5.4. The variational principle for eigenvalues of $\hat{\mathcal{R}}(E)$

In the last example, we shall use the Rayleigh–Ritz trial functions in the variational principle for eigenvalues of the operator $\hat{\mathcal{R}}(E)$. Substitution of the trial eigenfunction (186) to the functional (74) gives

$$F[\boldsymbol{c}^\dagger, \boldsymbol{c}] = \frac{\boldsymbol{c}^\dagger \mathbf{T} \boldsymbol{c}}{\boldsymbol{c}^\dagger \mathbf{N} \boldsymbol{c}} \tag{196}$$

where $\mathbf{T}$ is a Hermitean $N \times N$ matrix with elements defined by equation (178) and $\mathbf{N}$ is a Hermitean $N \times N$ overlap matrix with elements

$$N_{ij} = (\nabla_n \phi_i | \nabla_n \phi_j). \tag{197}$$

It must be emphasized that, even if we use the same coordinate functions as in the preceding subsection, the rank of the matrix $\mathbf{N}$ may differ from the rank of the matrix $\mathbf{M}$ used there. The condition

$$\delta F[\boldsymbol{c}^\dagger, \boldsymbol{c}] = 0 \tag{198}$$

gives generalized matrix eigenvalue problems

$$\mathbf{T}\boldsymbol{c} = \widetilde{b^{-1}} \mathbf{N} \boldsymbol{c} \qquad \boldsymbol{c}^\dagger \mathbf{T} = \widetilde{b^{-1}} \boldsymbol{c}^\dagger \mathbf{N} \tag{199}$$

where an eigenvalue

$$\widetilde{b^{-1}} = \frac{\boldsymbol{c}^\dagger \mathbf{T} \boldsymbol{c}}{\boldsymbol{c}^\dagger \mathbf{N} \boldsymbol{c}} \tag{200}$$

is a variational estimate of some eigenvalue of the operator $\hat{\mathcal{R}}(E)$. The number of non-trivial solutions of equations (199) equals the rank of the matrix $\mathbf{N}$. If $\widetilde{b_k^{-1}}$ and c_{ik} denote, respectively, a kth eigenvalue of the problem (199) and an ith component of the corresponding right eigenvector $\boldsymbol{c}_k$, in analogy with the spectral expansions (25) and (27) we have approximations of the kernels $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$ and $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$

$$\tilde{\mathcal{B}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{i,j=1}^{N} \phi_i(\boldsymbol{\rho}) \left[\sum_{k=1}^{\operatorname{rank} \mathbf{N}} c_{ik} \left(\widetilde{b_k^{-1}} \right)^{-1} c_{jk}^* \right] \phi_j^*(\boldsymbol{\rho}') \tag{201}$$

and

$$\tilde{\mathcal{R}}(E, \boldsymbol{\rho}, \boldsymbol{\rho}') = \sum_{i,j=1}^{N} \phi_i(\boldsymbol{\rho}) \left[\sum_{k=1}^{\operatorname{rank} \mathbf{N}} c_{ik} \widetilde{b_k^{-1}} c_{jk}^* \right] \phi_j^*(\boldsymbol{\rho}'). \tag{202}$$

As in the case discussed in the preceding subsection, these approximations are correct only to first order.

We emphasize that even if the set of the coordinate functions $\{\phi_i(\boldsymbol{r})\}$ used in the current discussion is the same as the set used in section 5.3, in general the kernels (194) and (201) will be *different* approximations of the kernel $\mathcal{B}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$. Similarly, the kernels (195) and (202) will be *different* approximations of the kernel $\mathcal{R}(E, \boldsymbol{\rho}, \boldsymbol{\rho}')$.

6. Concluding remarks

We have derived variational principles related to the non-relativistic R-matrix theory, namely for eigenvalues of the integral operators $\hat{\mathcal{R}}(E)$ and $\hat{\mathcal{B}}(E)$, for matrix elements of these operators and their reciprocals. Some of the principles were already known but others seem to be new. The essential result is that *all* these principles may be constructed, *in a systematic way*, by using the approach of Gerjuoy *et al* [50].

Apart from the variational principles constructed here, there exists a variety of other variational principles for eigenvalues and matrix elements of the operators $\hat{\mathcal{R}}(E)$ and $\hat{\mathcal{B}}(E)$ which might be derived by minor modifications of considerations presented in sections 3 and 4. For instance, alternative variational principles for eigenvalues of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ are

$$b(E) = \text{stat}\left\{\frac{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}{(\overline{\Psi}|\nabla_n\overline{\Psi})}\left[\frac{(\overline{\Psi}|\nabla_n\overline{\Psi})}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})} + \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}\rangle}{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}\right]\frac{(\nabla_n\overline{\Psi}|\nabla_n\overline{\Psi})}{(\nabla_n\overline{\Psi}|\overline{\Psi})}\right\} \tag{203}$$

and

$$b^{-1}(E) = \text{stat}\left\{\frac{(\overline{\Psi}|\overline{\Psi})}{(\overline{\Psi}|\nabla_n\overline{\Psi})}\left[\frac{(\nabla_n\overline{\Psi}|\overline{\Psi})}{(\overline{\Psi}|\overline{\Psi})} - \frac{2m}{\hbar^2}\frac{\langle\overline{\Psi}|[\hat{H}-E]\overline{\Psi}\rangle}{(\overline{\Psi}|\overline{\Psi})}\right]\frac{(\overline{\Psi}|\overline{\Psi})}{(\nabla_n\overline{\Psi}|\overline{\Psi})}\right\} \tag{204}$$

(cf equations (52) and (76), respectively). The variational principles constructed in sections 3 and 4 are, however, optimal in two respects. First, the functionals derived seem to be the simplest possible (cf the functionals in equations (52) and (76) with those in equations (203) and (204)). Secondly, these functionals have desirable symmetry properties: estimates of real eigenvalues $b_i(E)$ and $b_i^{-1}(E)$ obtained with arbitrary trial functions are real and matrices formed from variational estimates of matrix elements of the Hermitean operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ are also Hermitean. These properties of functionals are by no means guaranteed by the Hermicity of the operators only and, for instance, one might easily construct variational principles such that, although stationary values of functionals used would be real eigenvalues of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$, variational estimates obtained would be, in general, complex. It is clear that such variational principles would be of little practical importance.

In the second part of this paper [52] we shall derive variational principles related to the R-matrix theory of particles described by the Dirac equation [57, 58].

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Appendix. Some properties of determinants

Assume that a square $N \times N$ matrix $\mathbf{M}$ may be partitioned into

$$\mathbf{M} = \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} \tag{205}$$

where $\mathbf{A}$ and $\mathbf{D}$ are square $m \times m$ and $n \times n$ matrices, respectively, while $\mathbf{B}$ and $\mathbf{C}$ are rectangular $n \times m$ and $m \times n$ matrices, respectively. Here $0 < m, n < N$ and $m + n = N$. We presume that the matrix $\mathbf{A}$ is nonsingular and, therefore, has an inverse. We wish to find the determinant of the matrix $\mathbf{M}$. To this end we notice that the determinant of the upper triangular matrix

$$\mathbf{N} = \begin{pmatrix} \mathbf{I}_m & \mathbf{X} \\ \mathbf{0} & \mathbf{I}_n \end{pmatrix} \tag{206}$$

where $\mathbf{I}_m$ and $\mathbf{I}_n$ are unit $m \times m$ and $n \times n$ matrices, respectively, is

$$\det \mathbf{N} = 1 \tag{207}$$

irrespective of the form of the rectangular $n \times m$ matrix $\mathbf{X}$. Thus we may write

$$\det \mathbf{M} = \det \mathbf{M} \cdot \det \mathbf{N} = \det \mathbf{MN} = \det \left\{ \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{pmatrix} \begin{pmatrix} \mathbf{I}_m & \mathbf{X} \\ \mathbf{0} & \mathbf{I}_n \end{pmatrix} \right\}$$

$$= \det \begin{pmatrix} \mathbf{A} & \mathbf{AX} + \mathbf{B} \\ \mathbf{C} & \mathbf{CX} + \mathbf{D} \end{pmatrix}. \tag{208}$$

We observe that the expression for $\det \mathbf{M}$ obtained contains a free 'parameter', the matrix $\mathbf{X}$, which we may choose at our will. We utilize this fact and impose the condition

$$\mathbf{AX} + \mathbf{B} = \mathbf{0} \tag{209}$$

hence

$$\mathbf{X} = -\mathbf{A}^{-1}\mathbf{B}. \tag{210}$$

With this particular choice of $\mathbf{X}$ we have

$$\det \mathbf{M} = \det \begin{pmatrix} \mathbf{A} & \mathbf{0} \\ \mathbf{C} & \mathbf{D} - \mathbf{CA}^{-1}\mathbf{B} \end{pmatrix} = \det \mathbf{A} \cdot \det(\mathbf{D} - \mathbf{CA}^{-1}\mathbf{B}) \tag{211}$$

where the last equality follows from the well known property of determinants [59].

Consider now the very special case when $n = 1$. Then $\mathbf{A}$ is the $(N-1) \times (N-1)$ square matrix, $\mathbf{B}$ is the $(N-1) \times 1$ *column* matrix, $\mathbf{C}$ is the $1 \times (N-1)$ *row* matrix and $\mathbf{D}$ is the 1×1 matrix, i.e. a number. If $\mathbf{D} = 0$, we have

$$\det \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & 0 \end{pmatrix} = -\det \mathbf{A} \cdot \det(\mathbf{CA}^{-1}\mathbf{B}) = -(\det \mathbf{A}) \cdot \mathbf{CA}^{-1}\mathbf{B} \qquad n = 1 \tag{212}$$

where we have omitted the symbol det utilizing the fact that $\mathbf{CA}^{-1}\mathbf{B}$ is the 1×1 matrix, i.e. a number. Equation (212) implies

$$\mathbf{CA}^{-1}\mathbf{B} = -\frac{\det \begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & 0 \end{pmatrix}}{\det \mathbf{A}} \qquad n = 1 \tag{213}$$

the formula which we have used to derive equations (174), (175), (183) and (184).

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