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REGULAR ARTICLE

A Hartree–Fock approach to the Steklov eigenproblem for a two-electron atom in an s^2 state

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Abstract Two decades ago, in a brief note (Hinze and Hamacher, J Chem Phys 92:4372–4373, 1990), Hinze and Hamacher made a conjecture that the Hartree–Fock method may be applied to determine approximate solutions to a non-standard (Steklov-type) eigenproblem encountered in the non-relativistic eigenchannel *R*-matrix method. Later, this thread was mathematically pursued further by the present author (Szmytkowski, Phys Rev A 61:022725, 2000; erratum 66:029901, 2002). In the present paper, which is dedicated to the memory of Professor Jürgen Hinze, we make an attempt to elucidate the idea underlying the aforementioned works. To focus on the essence and avoid obscuring mathematical details, we consider the simplest system which is a two-electron atom in an s^2 state. Variational principles for pertinent Steklov eigenvalues (i.e., eigenvalues of a two-electron Dirichlet-to-Neumann integral operator) and for their reciprocals (i.e., eigenvalues of a two-electron Neumann-to-Dirichlet integral operator) are used to derive a radial integro-differential eigensystem of a Hartree–Fock type, in which both a Lagrange multiplier in an integro-differential equation and a Steklov eigenvalue appearing in a boundary condition are to be determined simultaneously at a fixed total energy of the atom. Mathematical similarities and (particularly) differences between the problem considered here and that of a spherically confined two-electron atom are highlighted.

Dedicated to the memory of Professor Jürgen Hinze and published as part of the Hinze Memorial Issue.

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1 Introduction

The eigenchannel approach to the *R*-matrix method was proposed in 1965 by Danos and Greiner [1] in the context of nuclear reaction physics. In the 1970s, Fano and Lee [2, 3] introduced this technique into atomic physics. Since then, the approach has proved its power in the analysis of complex Rydberg spectra and photoionization processes (cf, e.g., [4]).

Thus far, nearly all eigenchannel *R*-matrix studies were based on a configuration-interaction (CI) approach: a trial function approximating a many-electron eigenfunction within an *R*-matrix hypervolume was chosen as a linear combination (with coefficients to be optimized) of configuration state functions constructed from Slater determinants, the latter being built of *prescribed* single-electron spin-orbitals. The Kohn's variational principle for reciprocals of *R*-matrix eigenvalues [5] was used to optimize the combination coefficients.

In a brief paper [6] published two decades ago, Hinze and Hamacher pointed out that the aforementioned Kohn's principle might be used as a starting point for *simultaneous* optimization of the CI coefficients *and* spin-orbitals in approximate *R*-matrix eigenfunctions. In many respects, the technique proposed by these authors (developed further numerically by Hamacher in his thesis [7] and mathematically by the present author in Ref. [8]) for solving an underlying atomic Steklov-type eigenproblem is analogous to the multi-configuration Hartree–Fock (MCHF) method, nowadays routinely used for computation of atomic structures [9]. However, the analogy is not perfect and there are features which make the suggested MCHF eigenchannel *R*-matrix method technically more challenging (and mathematically more interesting) than its atomic-structure counterpart.

It is the purpose of the present paper to elucidate *the essential idea* underlying the works [6–8]. For the sake of clarity, we shall focus on the mathematically simplest, but still sufficiently representative, system which is a two-electron atom in an s^2 state.

The reader interested in an extension of the eigenchannel *R*-matrix formalism to relativistic atomic and molecular systems should consult Refs. [10, 11].

2 The atomic Steklov eigenproblem and properties of its solutions

Consider a non-relativistic two-electron atom with an infinitely heavy point-like and spinless nucleus of charge *Ze*. The Hamiltonian of the atom is

$$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}. \tag{1}$$

Let us divide the physical space $\mathbb{R}^3$ into two regions $\mathcal{V}$ and $\mathbb{R}^3 \setminus \mathcal{V}$, where $\mathcal{V}$ is a sphere of radius ρ centered at the atomic nucleus. The surface of the sphere $\mathcal{V}$ will be denoted by $\mathcal{S}$. With the sphere $\mathcal{V}$ one may associate a hypervolume $\mathfrak{V} = \mathcal{V} \times \mathcal{V} \subset \mathbb{R}^6$, bounded by the hypersurface $\mathfrak{S} = \mathfrak{S}_1 \cup \mathfrak{S}_2$ composed of two geometrically similar hyperfacets

$$\mathfrak{S}_1 = \mathcal{S}_1 \times \mathcal{V}_2, \qquad \mathfrak{S}_2 = \mathcal{V}_1 \times \mathcal{S}_2 \tag{2}$$

(the subscripts at $\mathcal{V}$ and $\mathcal{S}$ refer to particular electrons). A radius vector of a two-electron configuration in the hypervolume $\mathfrak{V}$ will be denoted by $\mathfrak{r}$. If the configuration point is on the hypersurface $\mathfrak{S}$, the symbol $\boldsymbol{\varrho}$ will be used instead of $\mathfrak{r}$.

If $\Phi(\mathfrak{r})$ and $\Phi'(\mathfrak{r})$ are sufficiently regular multicomponent functions defined in $\mathfrak{V}$ and on $\mathfrak{S}$, we define their scalar products over these domains as

$$\langle\Phi|\Phi'\rangle_{\mathfrak{V}} = \int_{\mathfrak{V}} d^6\mathfrak{r}\,\Phi^{\dagger}(\mathfrak{r})\Phi'(\mathfrak{r}) \tag{3}$$

and

$$\big(\Phi|\Phi'\big)_{\mathfrak{S}} = \oint_{\mathfrak{S}} d^5\boldsymbol{\varrho}\,\Phi^{\dagger}(\boldsymbol{\varrho})\Phi'(\boldsymbol{\varrho}), \tag{4}$$

respectively. Here, the dagger denotes the matrix Hermitian conjugation, while

$$\int_{\mathfrak{V}} d^6\mathfrak{r}(\cdots) = \int_{\mathcal{V}} d^3\boldsymbol{r}_1 \int_{\mathcal{V}} d^3\boldsymbol{r}_2(\cdots), \tag{5}$$

$$\oint_{\mathfrak{S}} d^5\boldsymbol{\varrho}(\cdots) = \oint_{\mathcal{S}} d^2\boldsymbol{\varrho}_1 \int_{\mathcal{V}} d^3\boldsymbol{r}_2(\cdots) + \int_{\mathcal{V}} d^3\boldsymbol{r}_1 \oint_{\mathcal{S}} d^2\boldsymbol{\varrho}_2(\cdots). \tag{6}$$

In the eigenchannel *R*-matrix method [8, 12, 13], one considers an eigenvalue problem consisting of the time-independent Schrödinger equation in the hypervolume $\mathfrak{V}$:

$$[\hat{\mathcal{H}} - E]\Psi_i(E,\mathfrak{r}) = 0 \qquad (\mathfrak{r} \in \mathfrak{V}) \tag{7}$$

and the boundary condition on the hypersurface $\mathfrak{S}$:

$$[\nabla_{\perp} - b_i(E)]\Psi_i(E,\boldsymbol{\varrho}) = 0 \qquad (\boldsymbol{\varrho} \in \mathfrak{S}), \tag{8}$$

where $\nabla_{\perp}$ stands for a normal derivative symbol at the point $\boldsymbol{\varrho}$ on the hypersurface $\mathfrak{S}$, E is a *fixed* real parameter (being the energy of the system) and $b_i(E)$ is an eigenvalue. To fulfill the Pauli principle, the eigenfunctions $\{\Psi_i(E,\mathfrak{r})\}$ are constrained to be antisymmetric with respect to permutations of the two atomic electrons. It may be shown [8] that all eigenvalues to this system are real and that eigenfunctions associated with different eigenvalues are orthogonal in the sense of

$$\big(\Psi_i|\Psi_j\big)_{\mathfrak{S}} = 0 \qquad (b_i(E) \neq b_j(E)). \tag{9}$$

Without any loss of generality, one may assume that any two *different* eigenfunctions obey

$$\big(\Psi_i|\Psi_j\big)_{\mathfrak{S}} = 0 \qquad (i \neq j). \tag{10}$$

It is to be noticed that the Steklov eigenvalue $b_i(E)$ has poles at these energies at which the surface part of the corresponding eigenfunction, $\Psi_i(E,\boldsymbol{\varrho})$, vanishes identically on $\mathfrak{S}$.

In mathematics, eigenproblems of the sort (7) and (8), in which an eigenvalue does not enter a differential equation but, instead, it appears in a boundary condition, are known as Steklov (Stekloff) eigenproblems [14–17].

It can be shown (cf., e.g., Refs. [8, 12, 13] and references therein) that eigenvalues to the eigenproblem (7) and (8) are stationary points of the Kohn functional

$$F^{(+)}[\bar{\Psi}] = \frac{\big(\bar{\Psi}|\nabla_{\perp}\bar{\Psi}\big)_{\mathfrak{S}}}{\big(\bar{\Psi}|\bar{\Psi}\big)_{\mathfrak{S}}} + \frac{2m}{\hbar^2}\frac{\langle\bar{\Psi}|[\hat{\mathcal{H}} - E]\bar{\Psi}\rangle_{\mathfrak{V}}}{\big(\bar{\Psi}|\bar{\Psi}\big)_{\mathfrak{S}}}, \tag{11}$$

while their reciprocals are stationary points of the functional

$$F^{(-)}[\bar{\Psi}] = \frac{\big(\nabla_{\perp}\bar{\Psi}|\bar{\Psi}\big)_{\mathfrak{S}}}{\big(\nabla_{\perp}\bar{\Psi}|\nabla_{\perp}\bar{\Psi}\big)_{\mathfrak{S}}} - \frac{2m}{\hbar^2}\frac{\langle\bar{\Psi}|[\hat{\mathcal{H}} - E]\bar{\Psi}\rangle_{\mathfrak{V}}}{\big(\nabla_{\perp}\bar{\Psi}|\nabla_{\perp}\bar{\Psi}\big)_{\mathfrak{S}}}, \tag{12}$$

provided the trial functions $\bar{\Psi}(\mathfrak{r})$ are varied freely in the whole functional space.

The importance of the eigensystem (7) and (8) lies in the fact that from its eigenvalues $\{b_i(E)\}$ and eigenfunctions $\{\Psi_i(E,\mathfrak{r})\}$ one constructs kernels

$$\mathcal{B}(E,\varrho,\varrho') = \sum_i \frac{\Psi_i(E,\varrho)b_i(E)\Psi_i^\dagger(E,\varrho')}{(\Psi_i|\Psi_i)_{\mathfrak{S}}} \tag{13}$$

and

$$\mathcal{R}(E,\varrho,\varrho') = \sum_i \frac{\Psi_i(E,\varrho)b_i^{-1}(E)\Psi_i^\dagger(E,\varrho')}{(\Psi_i|\Psi_i)_{\mathfrak{S}}} \tag{14}$$

of two mutually reciprocal energy-dependent integral operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$, such that for *any* function $\Psi(E,\mathfrak{r})$ which solves the equation

$$[\hat{\mathcal{H}} - E]\Psi(E,\mathfrak{r}) = 0 \qquad (\mathfrak{r} \in \mathfrak{V}) \tag{15}$$

it holds that

$$\nabla_\perp \Psi(E,\varrho) = \hat{\mathcal{B}}(E)\Psi(E,\varrho) \qquad (\varrho \in \mathfrak{S}) \tag{16}$$

and

$$\hat{\mathcal{R}}(E)\nabla_\perp \Psi(E,\varrho) = \Psi(E,\varrho) \qquad (\varrho \in \mathfrak{S}). \tag{17}$$

Equations (16) and (17) make evident why in mathematics $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ are called the Dirichlet-to-Neumann (DtN) and the Neumann-to-Dirichlet (NtD) operators, respectively (occasionally, the DtN operator is also named the Steklov or the Steklov–Poincaré operator).

Matrix representations of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ in any L^2 basis on the hypersurface $\mathfrak{S}$ are known as the log-derivative matrix $\mathsf{B}(E)$ and the R-matrix $\mathsf{R}(E)$, respectively. These two mutually reciprocal matrices are central objects in the R-matrix theory of quantum scattering [12].

As the Hamiltonian (1) is non-separable, the eigensystem (7) and (8) cannot be solved exactly and approximate methods have to be used. A particular approximate method, based on the idea of Hinze and Hamacher exposed in Ref. [6], will be presented below.

3 The Hartree–Fock approximation

In the rest of this work, we shall be interested in those eigensolutions to the Steklov eigensystem (7) and (8) which, in the central field limit, correspond to the electronic configuration s^2. We shall seek approximations to the pertinent eigenfunctions in the class of two-electron functions of the form

$$\begin{aligned}\bar{\Psi}_{\mathrm{s}^2}(E,\mathfrak{r}) = \bar{\varphi}(E,\boldsymbol{r}_1)\bar{\varphi}(E,\boldsymbol{r}_2)\frac{1}{\sqrt{2}}[\chi_\uparrow(1)\otimes\chi_\downarrow(2) \\ - \chi_\downarrow(1)\otimes\chi_\uparrow(2)],\end{aligned} \tag{18}$$

where $\chi_\uparrow$ and $\chi_\downarrow$ are the standard orthonormal electronic spin eigenfunctions, $\otimes$ denotes the Kronecker's direct matrix product, while the spatial orbital is

$$\bar{\varphi}(E,\boldsymbol{r}) = \frac{1}{r}\bar{P}(E,r)Y_{00}(\boldsymbol{r}/r), \tag{19}$$

with $Y_{00}(\boldsymbol{r}/r) = 1/\sqrt{4\pi}$. We subject the function $\bar{P}(E,r)$ to the constraint

$$\bar{P}(E,0) = 0 \tag{20}$$

and, for convenience, impose the normalization condition

$$\int_0^\rho \mathrm{d}r\bar{P}^2(E,r) = 1. \tag{21}$$

Otherwise, at this stage, the function $\bar{P}(E,r)$ remains unspecified, and in Sects. 4 and 5, we shall use suitably modified functionals from Sect. 2 to determine its optimal form (or, possibly, forms, as two functionals will be in use).

4 Application of the variational principle for Steklov eigenvalues

In this section, we shall optimize the radial function $\bar{P}(E,r)$ and find an approximation to the Steklov eigenvalue $b_{\mathrm{s}^2}(E)$ with the help of a variational principle based on the functional (11).

We begin with the observation that if the function (18) is to be used as a variational trial function, the functional (11) has to be modified in order to build in the normalization constraint (21) (the constraint (20) needs not to be incorporated explicitly). The properly modified functional is

$$\begin{aligned}F^{(+)}[\bar{P},\bar{\varepsilon}] = \frac{(\bar{\Psi}|\nabla_\perp\bar{\Psi})_{\mathfrak{S}}}{(\bar{\Psi}|\bar{\Psi})_{\mathfrak{S}}} + \frac{2m}{\hbar^2}\frac{\langle\bar{\Psi}|[\hat{\mathcal{H}}-E]\bar{\Psi}\rangle_{\mathfrak{V}}}{(\bar{\Psi}|\bar{\Psi})_{\mathfrak{S}}} \\ - \frac{2m}{\hbar^2}\frac{\bar{\varepsilon}(E)\left[\int_0^\rho \mathrm{d}r\bar{P}^2(E,r) - 1\right]}{\bar{P}^2(E,\rho)},\end{aligned} \tag{22}$$

where $\bar{\varepsilon}(E)$ is a Lagrange multiplier, optimal value of which (designated hereafter as $\varepsilon(E)$) has to be determined simultaneously with the optimal form $P(E,r)$ of $\bar{P}(E,r)$.

Substitution of the trial function (18) into the right-hand side of Eq. (22) and integration over angular variables transforms the functional into

$$\begin{aligned}F^{(+)}[\bar{P},\bar{\varepsilon}] = -\frac{1}{\rho} + \frac{\bar{P}'(E,\rho)}{\bar{P}(E,\rho)} \\ + \frac{2m}{\hbar^2}\frac{\int_0^\rho \mathrm{d}r\bar{P}(E,r)\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{Ze^2}{r}\right]\bar{P}(E,r) - \frac{1}{2}E}{\bar{P}^2(E,\rho)} \\ + \frac{2m}{\hbar^2}\frac{\frac{1}{2}e^2\int\limits_0^\rho \mathrm{d}r\int\limits_0^\rho \mathrm{d}r'\frac{\bar{P}^2(E,r)\bar{P}^2(E,r')}{r_>}}{\bar{P}^2(E,\rho)} \\ - \frac{2m}{\hbar^2}\frac{\bar{\varepsilon}(E)\left[\int_0^\rho \mathrm{d}r\bar{P}^2(E,r) - 1\right]}{\bar{P}^2(E,\rho)},\end{aligned} \tag{23}$$

where $r_> = \max(r, r')$ and

$$\bar{P}'(E,\rho) = \left.\frac{\mathrm{d}\bar{P}(E,r)}{\mathrm{d}r}\right|_{r=\rho}. \tag{24}$$

The first variation of $F^{(+)}$ due to small variations in $\bar{P}(E,r)$ and $\bar{\varepsilon}(E)$ around $P(E, r)$ and $\varepsilon(E)$, respectively, is given by

$$\begin{aligned} &P^2(E,\rho)\delta F^{(+)}[P,\varepsilon] \\ &= 2\left[P'(E,\rho) - \left(F^{(+)}[P,\varepsilon] + \frac{1}{\rho}\right)P(E,\rho)\right]\delta P(E,\rho) \\ &+ 2\frac{2m}{\hbar^2}\int\limits_0^\rho \mathrm{d}r\delta P(E,r)\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{Ze^2}{r} + \frac{e^2}{r}Y_0(E,r) - \varepsilon(E)\right] \\ &\times P(E,r) - \frac{2m}{\hbar^2}\delta\varepsilon(E)\left[\int\limits_0^\rho \mathrm{d}rP^2(E,r) - 1\right], \end{aligned} \tag{25}$$

where

$$Y_0(E,r) = r\int\limits_0^\rho \mathrm{d}r'\frac{P^2(E,r')}{r_>} \tag{26}$$

is the Hartree integral.

We shall determine $P(E, r)$ and $\varepsilon(E)$ from the requirement that they make the functional (23) stationary, i.e.,

$$\delta F^{(+)}[P,\varepsilon] = 0. \tag{27}$$

Denoting

$$\widetilde{b}(E) = F^{(+)}[P,\varepsilon] \tag{28}$$

(the tilde reminds that $\widetilde{b}(E)$ is an *estimate* of the Steklov eigenvalue $b_{\mathrm{s}^2}(E)$), from Eqs. (25) and (27), we infer the normalization condition (21) for $P(E, r)$ (as we should) and the integro-differential equation

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{Ze^2}{r} + \frac{e^2}{r}Y_0(E,r) - \varepsilon(E)\right]P(E,r) = 0 \\ (0 \le r \le \rho), \tag{29}$$

together with the boundary condition at $r = \rho$:

$$P'(E,\rho) - \left(\widetilde{b}(E) + \frac{1}{\rho}\right)P(E,\rho) = 0. \tag{30}$$

The boundary condition at $r = 0$ follows from Eq. (20) and is

$$P(E,0) = 0. \tag{31}$$

The eigensystem (29)–(31) is still incomplete. The missing ingredient is obtained if one substitutes the optimal form of $\bar{P}(E,r)$, i.e., $P(E, r)$, and the corresponding optimal value of $\bar{\varepsilon}(E)$, i.e., $\varepsilon(E)$, into Eq. (23), making subsequently use of Eqs. (26), (29), (30) and (21) (the latter being specialized for $P(E, r)$). This yields

$$\begin{aligned} F^{(+)}[P,\varepsilon] &= \widetilde{b}(E) \\ &+ \frac{2m}{\hbar^2}\frac{\varepsilon(E) - \frac{1}{2}E - \frac{1}{2}\int_0^\rho \mathrm{d}r\frac{e^2}{r}Y_0(E,r)P^2(E,r)}{P^2(E,\rho)}, \end{aligned} \tag{32}$$

which, in virtue of Eq. (28), implies the following relation:

$$E - 2\varepsilon(E) + \int\limits_0^\rho \mathrm{d}r\frac{e^2}{r}Y_0(E,r)P^2(E,r) = 0 \tag{33}$$

constraining $P(E, r)$ and $\varepsilon(E)$. Equations (29)–(31) and (33), supplemented by the definition (26), constitute a *two-parameter* integro-differential eigenproblem, with the Lagrange multiplier $\varepsilon(E)$ and the Steklov parameter $\widetilde{b}(E)$ being eigenvalues.

5 Application of the variational principle for reciprocals of Steklov eigenvalues

Considerations analogous to those presented in Sect. 4 may be carried out if one starts from the following suitable modification of the functional (12):

$$\begin{aligned} F^{(-)}[\bar{P},\bar{\varepsilon}] = &\frac{\left(\nabla_\perp\bar{\Psi}\middle|\bar{\Psi}\right)_{\mathfrak{S}}}{\left(\nabla_\perp\bar{\Psi}\middle|\nabla_\perp\bar{\Psi}\right)_{\mathfrak{S}}} - \frac{2m}{\hbar^2}\frac{\langle\bar{\Psi}|[\hat{\mathcal{H}} - E]\bar{\Psi}\rangle_{\mathfrak{V}}}{\left(\nabla_\perp\bar{\Psi}\middle|\nabla_\perp\bar{\Psi}\right)_{\mathfrak{S}}} \\ &+ \frac{2m}{\hbar^2}\frac{\bar{\varepsilon}(E)\left[\int_0^\rho \mathrm{d}r\bar{P}^2(E,r) - 1\right]}{\left[\bar{P}'(E,\rho) - \rho^{-1}\bar{P}(E,\rho)\right]^2}, \end{aligned} \tag{34}$$

where $\bar{\varepsilon}(E)$ is a Lagrange multiplier. Substitution of the trial function (18) to the functional (34) gives

$$\begin{aligned} F^{(-)}[\bar{P},\bar{\varepsilon}] = &\frac{\bar{P}(E,\rho)}{\bar{P}'(E,\rho) - \rho^{-1}\bar{P}(E,\rho)} \\ &- \frac{2m}{\hbar^2}\frac{\int_0^\rho \mathrm{d}r\bar{P}(E,r)\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{Ze^2}{r}\right]\bar{P}(E,r) - \frac{1}{2}E}{\left[\bar{P}'(E,\rho) - \rho^{-1}\bar{P}(E,\rho)\right]^2} \\ &- \frac{2m}{\hbar^2}\frac{\frac{1}{2}e^2\int_0^\rho \mathrm{d}r\int_0^\rho \mathrm{d}r'\frac{\bar{P}^2(E,r)\bar{P}^2(E,r')}{r_>}}{\left[\bar{P}'(E,\rho) - \rho^{-1}\bar{P}(E,\rho)\right]^2} \\ &+ \frac{2m}{\hbar^2}\frac{\bar{\varepsilon}(E)\left[\int_0^\rho \mathrm{d}r\bar{P}^2(E,r) - 1\right]}{\left[\bar{P}'(E,\rho) - \rho^{-1}\bar{P}(E,\rho)\right]^2}. \end{aligned} \tag{35}$$

On varying $F^{(-)}$, requiring

$$\delta F^{(-)}[P,\varepsilon] = 0 \tag{36}$$

and denoting

$$\widetilde{b^{-1}}(E) = F^{(-)}[P,\varepsilon], \tag{37}$$

we infer the integro-differential equation

$$\left[-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{Ze^2}{r} + \frac{e^2}{r}Y_0(E,r) - \varepsilon(E)\right]P(E,r) = 0 \\ (0 \le r \le \rho), \tag{38}$$

with $Y_0(E, r)$ defined in Eq. (26), the normalization constraint (21) (now specialized for $P(E, r)$) and also the boundary condition

$$P'(E,\rho) - \left(\frac{1}{\widetilde{b^{-1}}(E)} + \frac{1}{\rho}\right)P(E,\rho) = 0. \tag{39}$$

These are to be augmented by the boundary condition

$$P(E,0) = 0, \tag{40}$$

which follows from Eq. (20). In addition, on evaluating $F^{(-)}[P, \varepsilon]$ with the aid of Eqs. (35) and (37)–(39), we deduce

$$E - 2\varepsilon(E) + \int_0^\rho \mathrm{d}r \frac{e^2}{r} Y_0(E,r) P^2(E,r) = 0. \tag{41}$$

Comparison of the eigensystem (38)–(41) with the eigensystem (29)–(31) and (33) shows that they are *identical* and that it must hold that

$$\widetilde{b^{-1}}(E) = \widetilde{b}^{-1}(E) \tag{42}$$

This by no means trivial result justifies *a posteriori* the use of the same symbols for optimal radial eigenfunctions $P(E, r)$ and Lagrange multipliers $\varepsilon(E)$ in both eigensystems.

6 Concluding remarks

The reader familiar with nowadays trendy subject of confined quantum systems [18–22] recognizes immediately in Eqs. (29) and (38) the radial Hartree–Fock equation for a two-electron closed-shell (s^2) atom confined to the interior of the sphere $\mathcal{V}$, with a nucleus located at the center of $\mathcal{V}$. There are, however, two marked differences between the standard confined atom problem and the present one. First, the standard problem is a single-eigenvalue eigenproblem in which the boundary condition at $r = \rho$ is prescribed (as $P(\rho) = 0$) and the only eigenvalue is the Lagrange multiplier ε. On the contrary, in the present case, the parameter $\widetilde{b}(E)$ in the boundary condition (30) is an eigenvalue as well and is to be determined simultaneously with $\varepsilon(E)$. Second, while in the standard problem, Eq. (32) is secondary and serves for determination of the total energy once the Lagrange multiplier and the corresponding radial eigenfunction have been found, in the present case, where E is known *in advance*, this equation is one of the constituents of the *two*-parameter eigensystem. These features make the problem of solving the eigensystem (29)–(31) and (33) a non-trivial (but nevertheless feasible, cf. Ref. [7]) one.

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