Models of two-electron composite quantum systems

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ABSTRACT

Aimed at applications to the photonics of composite two-electron quantum systems like a helium atom in hyperspherical coordinates, the boundary value problem (BVP) for a system of coupled self-adjoined 3D elliptic partial differential equations of the Schrödinger type with homogeneous third-type boundary conditions is formulated in coupled-channel adiabatic approach. The Kantorovich reduction of the problem to BVPs for ordinary second-order differential equations (ODEs) with respect to functions of a single hyperradial variable is implemented by expanding the solution over a set of surface (angular) functions that depend on the hyperradial variable as a parameter. Benchmark calculations are presented by the example of the ground and first excited states of a Helium atom. The convergence of the results with respect to the number of the surface functions and their components is studied. The comparison with the known results is presented.

Keywords: Helium-like atom, boundary value problem, Schrödinger equation, hyperspherical coordinates, coupled-channel adiabatic approach, Kantorovich method

1. INTRODUCTON

Mathematical models of composite quantum systems in molecular, atomic and nuclear physics, as well as in physics of semiconductor nanostructures are described by boundary value problems (BVPs) for the multidimensional elliptic partial differential equations (PDEs) of the Schrödinger type in the configuration space $\mathbf{R}^d$. Such models are used in the studies of spectral and optical characteristics of excited states of a Helium-like atom,[1–19] photoionization and recombination of oppositely charged particles (positrons, antiprotons) in the magnet-optical trap,[20–22] optical absorption in quantum wells, quantum wires,[23] and quantum dots,[24,25] channeling of similarly charged particles in thin doped films[26] and resonance tunneling of composite systems through repulsive barriers,[27–30] photoionization of helium like atoms,[31] single-photon ionization of atoms[32] and photodissociation of molecules in a strong laser field.[33]

In the coupled-channel adiabatic approach (CCAA),[2,34] known in mathematical physics as the Kantorovich method (KM),[35] which widely apply for solving the above class of problems,[36] the desirable solution of the original BVP is expanded over surface eigenfunctions of the fast variables (e.g., the angular variables) of an auxiliary BVP for the appropriate PDE depending on a slow variable (for example, the radial variable) as a parameter. Averaging of the original BVP over the surface eigenfunctions leads to a 1D BVP for a system of coupled second-order ordinary differential equations (SOODEs) containing the potential matrix elements and the first-derivative coupling terms that are integrals of the products of the surface eigenfunctions and/or the first derivatives of the surface eigenfunctions with respect to a parameter (see, e.g.,[2,20]). As it was shown in previous papers[12,14–16,37] the key problem of application of this approach is such formulation of the BVP that provides calculation with required accuracy as matrix elements, as eigenvalues and radial vector-functions of SOODEs with using reasonable computer recourse.

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The aim of this paper is to present the convenient formulation of the problem stated above and the new efficient methods, algorithms, and programs for solving this problem, together with benchmark calculations.

We apply the finite-element procedure based on the use of high-order accuracy approximations for calculating the eigenvalues, surface eigenfunctions and their first derivatives with respect to a parameter of the parametric BVP for system of coupled self-adjoined 2D PDEs with the Dirichlet and/or Neumann-type boundary conditions in a finite 2D region, which arise when the BVP for system of coupled self-adjoined 3D PDEs is reduced to the 1D BVP for a system of coupled SOODEs in the framework of CCAA.[37] The program developed calculates the potential matrix elements that are integrals of the products of the surface eigenfunctions and/or the first derivatives of the surface eigenfunctions with respect to a parameter. These eigenvalues and potential matrix elements can be used for solving the bound-state and multi-channel scattering problems for a system of the coupled SOODEs with the help of the KANTBP programs.[38,39]

We seek for the solution of the parametric BVP for a system of coupled self-adjoined 2D PDEs in the form of expansion in the basis functions of the auxiliary Sturm-Liouville problem with respect to one of the fast variables. They are chosen in the analytical form or calculated by the ODPEVP program.[40] The coefficients of the expansion are vector-eigenfunctions of the parametric homogeneous 1D BVP for a system of the coupled SOODEs obtained by averaging the original BVP for system of coupled self-adjoined 2D PDEs over the basis functions. The first derivatives with respect to the parameter of these vector-eigenfunctions and eigenvalues are solutions of the parametric inhomogeneous 1D BVP, obtained by taking a derivative of the parametric homogeneous 1D BVP with respect to the parameter.[12] Then we solve the reduced parametric homogeneous and inhomogeneous 1D BVPs by means of the finite-element method using high-order accuracy approximations.[40] The generalized algebraic eigenvalue problem $\mathbf{A}\,\mathbf{F} = E\,\mathbf{B}\,\mathbf{F}$ with respect to a pair of unknowns $(E, \mathbf{F})$, arising after the replacing the differential problem with the finite-element approximation, is solved using the subspace iteration method implemented in the SSPACE program.[41] The first derivatives of the vector-eigenfunctions and eigenvalues with respect to the parameter are obtained by solving the inhomogeneous algebraic equations in accordance with the algorithm used in.[37,40] Finally, we evaluate the desirable matrix elements using the calculated eigenvalues, vector-eigenfunctions and their derivatives, which can be applied to generate the coupled system of slow-variable equations in the CCAA.

Benchmark calculations of the matrix elements, eigenvalues and eigenfunctions of the ground and first excited states of a Helium atom in the framework of a coupled-channel hyperspherical adiabatic approach are presented. The convergence of the matrix elements and eigenvalues with respect to both the number of the parametric vector-eigenfunctions and the number of their components is studied.

The structure of the paper is as follows. In Section 2 we present the statement of the problem and the formulation of the BVP for a system of coupled PDEs. In Sections 3 and 4 the reduction of the 3D and 2D BVPs to the 1D BVPs is described. In Section 5 the inhomogeneous parametric 1D BVP and the reduced matrix elements are derived. In Section 6 the benchmark calculations of matrix elements and the eigensolutions of the ground and the first exited states of a Helium atom in the framework of a coupled-channel hyperspherical adiabatic approach are analyzed. In Section 7 the results and the convergence of the expansions are discussed.

2. THE PROBLEM STATEMENT

We consider the model of a two-electron composite system like a helium atom in the rotating frame xyz with the z axis directed along the radius-vector $\mathbf{r_2}$ of the second electron in the configuration space $\mathbf{R}^6 \setminus 0$ spanned on the radius-vectors $\mathbf{r}_1 = \{r_1, \theta_1, \phi_1\}$ and $\mathbf{r}_2 = \{r_2, \theta_2, \phi_2\}$ of the electrons. The vector-function $\{\Psi_m^{Jm_J\sigma}(R, \alpha, \phi)\}_{m=(1-\sigma)/2}^{J}$ is characterized with the quantum numbers of the total angular momentum J, its third projection m_J onto the Z axis of the space-fixed frame, the set of its third projections $m = m(\sigma) = (1 - \sigma)/2, ..., J$ onto the z axis of the rotating frame, and the total parity $\lambda = p_t = \sigma(-)^J$, where $\sigma = \pm 1$ is the positive (or negative) reflection parity in the yz plane: $\phi \to \pi - \phi$, where ϕ is the rotation angle around the z axis. In hyperspherical coordinates $R = \sqrt{r_1^2 + r_2^2}, R \in [0, +\infty)$, $\tan\alpha/2 = r_1/r_2$, $\alpha \in [0, \pi]$, $\cos\theta = (\mathbf{r_1}\mathbf{r_2})/|\mathbf{r_1}||\mathbf{r_2}|\,\theta \in [0, \pi]$ using the atomic units the Schrödinger equation describing a helium-like atom with infinitely heavy mass of the

nucleus can be written as a BVP[12,42] with the following equation

$$\sum_{m'=m(\sigma)}^{J}\left(-\delta_{mm'}\left(\frac{1}{R^5}\frac{\partial}{\partial R}R^5\frac{\partial}{\partial R}-2E\right)+\frac{4}{R^2}D^{J\sigma}_{mm'}(\theta,\alpha;R)\right)\Psi^{J\sigma}_{m'}(R,\alpha,\theta)=0, \tag{1}$$

$$D^{J\sigma}_{mm}(\theta,\alpha;R)=T(\theta,\alpha)+V_{mm}(\theta,\alpha)+V(\theta,\alpha;R)+V^{J\sigma}_{mm}(\theta,\alpha), \tag{2}$$

$$T(\theta,\alpha;R)=-\frac{1}{\sin^2(\alpha)}\left(\frac{\partial}{\partial\alpha}\sin^2(\alpha)\frac{\partial}{\partial\alpha}+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right),$$

$$V(\theta,\alpha;R)=\frac{R}{2}\left(-\frac{2}{\sin(\alpha/2)}-\frac{2}{\cos(\alpha/2)}+\frac{1}{\sqrt{1-\sin(\alpha)\cos(\theta)}}\right),$$

$$V_{mm}(\theta,\alpha)=\frac{m^2}{\sin^2(\alpha)\sin^2(\theta)},\ V^{J\sigma}_{mm}(\alpha)=\frac{1}{4}\frac{J(J+1)-2m^2}{\cos^2(\alpha/2)},$$

$$D^{J\sigma}_{mm'}(\theta,\alpha;R)=\frac{1}{4}\frac{\gamma^{J\sigma}_{mm\pm1}}{\cos^2(\alpha/2)}\left(\pm\frac{\partial}{\partial\theta}+(m\pm1)\cot(\theta)\right)\delta_{m,m'=m\pm1},$$

$$\gamma^{J\sigma}_{mm+1}=-[1+(\sqrt{2}-1)\delta_{m0}][(J+m+1)(J-m)]^{1/2},$$

$$\gamma^{J\sigma}_{mm-1}=-[1+(\sqrt{2}-1)\delta_{m1}][(J-m+1)(J+m)]^{1/2}.$$

In the case of two-electron composite systems like a negative hydrogen ion in uniform magnetic field[19] (with strength $\gamma=B/B_0$, where $B_0=2.35\cdot10^5$T) one will add additional confinement potential $D^{J\sigma;\mathrm{conf}}_{mm'}(\theta,\alpha;R)$.

The total wave function $\Psi(R,\alpha,\theta)$ satisfies the following boundary conditions:

$$\lim_{R\to0}R^5\frac{\partial\Psi^{J\sigma}_{m=0}(R,\alpha,\theta)}{\partial R}=0,\quad \lim_{R\to0}\Psi^{J\sigma}_{m\neq0}(R,\alpha,\theta)=0,$$

$$\lim_{R\to\infty}R^5\Psi^{J\sigma}_{m}(R,\alpha,\theta)=0,\quad \lim_{\alpha\to0,\pi}\sin^2(\alpha)\frac{\partial\Psi^{J\sigma}_{m}(R,\alpha,\theta)}{\partial\alpha}=0, \tag{3}$$

$$\lim_{\theta\to0,\pi}\sin(\theta)\frac{\partial\Psi^{J\sigma}_{m=0}(R,\alpha,\theta)}{\partial\theta}=0,\quad \lim_{\theta\to0,\pi}\Psi^{J\sigma}_{m\neq0}(R,\alpha,\theta)=0$$

and is normalized by the condition

$$\sum_{m'=m(\sigma)}^{J}\int_0^\infty dRR^5\int_0^\pi d\alpha\sin^2(\alpha)\int_0^\pi d\theta\sin(\theta)\Psi^{J\sigma}_{mi}(R,\alpha,\theta)\Psi^{J\sigma}_{mj}(R,\alpha,\theta)=\delta_{ij}. \tag{4}$$

3. REDUCING THE 3D BVP TO A 1D BVP: THE KANTOROVICH EXPANSION

Consider the formal expansion of the solution of Eqs. (1)–(4) over set of two-dimensional parametric basis vector-functions $\{B_{mi}(\alpha,\theta;R)\}_{i=1}^{N}$ $(N\to\infty)$:

$$\Psi^{J\sigma}_{m}(R,\alpha,\theta)=\sum_{j=1}^{N}B^{J\sigma}_{mj}(\theta,\alpha;R)\chi^{J\sigma}_{j}(R). \tag{5}$$

In Eq. (5) the functions $\boldsymbol{\chi}^{J\sigma}(R)=\left(\chi^{J\sigma}_1(R),\chi^{J\sigma}_2(R),\ldots,\chi^{J\sigma}_N(R)\right)^T$ are unknown, and the adiabatic functions $\mathbf{B}^{J\sigma}_{m}(\theta,\alpha;R)=\left(B^{J\sigma}_{m1}(\alpha,\theta;R),B^{J\sigma}_{m2}(\theta,\alpha;R),\ldots,B^{J\sigma}_{mN}(\theta,\alpha;R)\right)^T$ form an orthonormal basis for each value of the hyperradius R which is treated here as a slowly varying adiabatic parameter.

After minimizing the Rayleigh-Ritz variational functional (see[12]), and using the expansion (5), the 3D BVP Eq. (1)– (4) is reduced to a finite set of N coupled SOODEs for $\boldsymbol{\chi}^{J\sigma}(R)$

$$\left(-\frac{1}{R^5}\mathbf{I}\frac{d}{dR}R^5\frac{d}{dR}+\mathbf{U}^{\mathbf{J}\sigma}(R)+\mathbf{Q}(R)\frac{d}{dR}+\frac{1}{R^5}\frac{dR^5\mathbf{Q}(R)}{dR}-2E\,\mathbf{I}\right)\boldsymbol{\chi}^{J\sigma}(R)=0, \tag{6}$$

$$\lim_{R\to0}R^5\frac{d\boldsymbol{\chi}^{J=0\sigma}(R)}{dR}=0,\quad \lim_{R\to0}\boldsymbol{\chi}^{J\neq0\sigma}(R)=0,\quad \lim_{R\to\infty}R^5\boldsymbol{\chi}^{J\sigma}(R)=0. \tag{7}$$

Here $\mathbf{I}$, $\mathbf{U}(R)$ and $\mathbf{Q}(R)$ are $N \times N$ matrices:

$$I_{ij} = \delta_{ij}, U_{ij}^{J\sigma}(R) = U_{ji}^{J\sigma}(R) = 2\frac{\varepsilon_i^{J\sigma}(R) + \varepsilon_j^{J\sigma}(R)}{R^2}\delta_{ij} + H_{ij}(R) \tag{8}$$

$$H_{ij}(R){=}H_{ji}(R){=} \sum_{m=m(\sigma)}^{J} \int_0^{\pi} d\alpha \sin^2(\alpha) \int_0^{\pi} d\theta \sin(\theta) \frac{\partial B_{mi}^{J\sigma}(\theta,\alpha;R)}{\partial R} \frac{\partial B_{mj}^{J\sigma}(\theta,\alpha;R)}{\partial R},$$

$$Q_{ij}(R){=}{-}Q_{ji}(R){=}{-} \sum_{m=m(\sigma)}^{J} \int_0^{\pi} d\alpha \sin^2(\alpha) \int_0^{\pi} d\theta \sin(\theta) B_{mi}^{J\sigma}(\theta,\alpha;R) \frac{\partial B_{mj}^{J\sigma}(\theta,\alpha;R)}{\partial R}.$$

This problem can be solved by means of FEM at the values R belonging to the Gaussian nodes of a finite-element grid Ω_R with the help of KANTBP programs.[38,39,43] In the KM[35,36] the parametric basis functions $B_i(\theta,\alpha;R)$ are defined as solutions of the following parametric BVP:

$$\sum_{m'=m(\sigma)}^{J} \left[\delta_{mm'} \left(D_{mm'}^{J\sigma}(\alpha,\theta;R) - \varepsilon_i^{J\sigma}(R) \right) + D_{mm'}^{J\sigma}(\alpha,\theta;R) \right] B_{m'i}^{J\sigma}(\theta,\alpha;R) = 0, \tag{9}$$

$$\lim_{\alpha\to 0,\pi} \sin^2(\alpha) \frac{\partial B_{mi}^{J\sigma}(\theta,\alpha;R)}{\partial \alpha} = 0, \quad \lim_{\theta\to 0,\pi} \sin(\theta) \frac{\partial B_{m=0i}^{J\sigma}(\theta,\alpha;R)}{\partial \theta} = 0, \quad \lim_{\theta\to 0,\pi} B_{m\neq 0i}^{J\sigma}(\theta,\alpha;R) = 0,$$

$$\sum_{m'=m(\sigma)}^{J} \int_0^{\pi} d\alpha \sin^2(\alpha) \int_0^{\pi} d\theta \sin(\theta) B_{mi}^{J\sigma}(\theta,\alpha;R) B_{mj}^{J\sigma}(\theta,\alpha;R) = \delta_{ij}, \tag{10}$$

where $D_{mm}^{J\sigma}(\alpha,\theta;R)$ and $D_{mm'}^{J\sigma}(\alpha,\theta;R)$ are determined by Eq. (2).

4. REDUCTION OF THE 2D PARAMETRIC BVP TO THE PARAMETRIC 1D BVP

Consider the following expansion of the adiabatic surface function $B_{mi}(\alpha,\theta;R)$:

$$B_{mi}^{J\sigma}(\theta,\alpha;R) = \sum_{j=m(\sigma)+1}^{j_{\max}} \psi_{mj}(\theta) \xi_{mj}^{(i)}(\alpha;R). \tag{11}$$

Here $\psi_{mj}(\theta) \equiv N_{j-1,m} P_{j-1+m}^{m}(\cos(\theta))$, $N_{j-1,m} = \{((2(j-1)+1)!/2)(j-1+m)!/(j-1)!\}^{1/2}$ is the normalized generalized Legendre polynomial:

$$-\frac{1}{\sin(\theta)} \frac{d}{d\theta} \sin(\theta) \frac{d\psi_{mj}(\theta)}{d\theta} + \frac{m^2 \psi_{mj}(\theta)}{\sin^2(\theta)} = \lambda_{mj} \psi_j(\theta), \quad \lambda_{mj} = (j+m)(j+m-1), \tag{12}$$

$$\lim_{\theta\to 0,\pi} \sin(\theta) \frac{d\psi_{0j}(\theta)}{d\theta} = 0, \ \psi_{m\neq 0,j}(\theta=0) = 0, \quad \psi_{m\neq 0,j}(\theta=\pi) = 0, \quad \int_0^{\pi} d\theta \sin(\theta) \psi_{mi}(\theta) \psi_{mj}(\theta) = \delta_{ij}.$$

After minimizing the variational functional we find that the eigenfunctions

$$\hat{\boldsymbol{\xi}}^{(i)}(\alpha;R) = \left\{ \boldsymbol{\xi}_m^{(i)}(\alpha;R) \right\}_{m=m(\sigma)}^{J}, \quad \boldsymbol{\xi}_m^{(i)}(\alpha;R) = \left(\xi_{m1}^{(i)}(\alpha;R), \xi_{m2}^{(i)}(\alpha;R), \ldots, \xi_{mj_{\max}}^{(i)}(\alpha;R) \right)^T$$

and eigenvalues $\varepsilon_i(R)$ satisfy the following eigenvalue problem for a set of $[(m(\sigma)+J)(j_{\max}-m(\sigma))]$ coupled SOODEs

$$\left(\hat{\mathbf{D}}(\alpha;R) - \varepsilon_i(R) \hat{\mathbf{I}} \right) \boldsymbol{\xi}^{(i)}(\alpha;R) = 0,$$

$$\sum_{m'=m(\sigma)}^{J} \sum_{j'=1+m(\sigma)}^{j_{\max}} \left[\delta_{mm'} \delta_{jj'} \left(D_{mjmj'}^{J\sigma}(\alpha;R) - \varepsilon_i^{J\sigma}(R) \right) + D_{mjm'j'}^{J\sigma}(\alpha;R) \right] \xi_{m'j'}^{(i)}(\alpha;R) = 0, \tag{13}$$

$$\lim_{\alpha\to 0,\pi} \sin^2(\alpha) \frac{\partial \xi_{mj'}^{(i)}(\alpha;R)}{\partial \alpha} = 0. \tag{14}$$

Here $\hat{\mathbf{I}} = \{\delta_{mm'}\mathbf{I}_{mm}\}_{m=m(\sigma)}^{J}$ and $\hat{\mathbf{D}}$, are symmetric $[(m(\sigma)+J)(j_{\max}-m(\sigma))] \times [(m(\sigma)+J)(j_{\max}-m(\sigma))]$ matrices with the following elements $D^{J\sigma}_{mjmj'}(\alpha;R)$:

$$\hat{I}_{ij} = \delta_{ij} = \sum_{m=m(\sigma)}^{J} \mathbf{I}_{mm}, \quad \mathbf{I}_{mm} = \int_0^{\pi} d\alpha \sin^2(\alpha) \left(\boldsymbol{\xi}_m^{(i)}(\alpha;R)\right)^T \boldsymbol{\xi}_m^{(j)}(\alpha;R), \tag{15}$$

$$D^{J\sigma}_{mimj}(\theta,\alpha;R) = T(\alpha;R)\delta_{ij} + W_{mimj}(\alpha;R) + V^{J\sigma}_{mm}(\alpha)\delta_{ij}, \quad W_{mimj}(\alpha;R) = RW_{mimj}(\alpha) \tag{16}$$

$$T(\alpha) = -\frac{1}{\sin^2(\alpha)}\left(\frac{\partial}{\partial\alpha}\sin^2(\alpha)\frac{\partial}{\partial\alpha}\right) + \left[\frac{\lambda_i+\lambda_j}{2\sin^2(\alpha)}\right],$$

$$W_{mimj}(\alpha) = +\left[\frac{1}{2}\left(-\frac{2}{\sin(\alpha/2)} - \frac{2}{\cos(\alpha/2)}\right)\right]\delta_{ij} + \frac{1}{2}W^{rep}_{mimj}(\alpha), \tag{17}$$

$$W^{rep}_{mimj}(\alpha) = W^{rep}_{mimj}(\pi-\alpha) = \int_0^{\pi} d\theta \sin(\theta)\frac{P^m_{i-1}(\cos(\theta))P^m_{j-1}(\cos(\theta))}{\sqrt{1-\sin(\alpha)\cos(\theta)}} = \int_{-1}^{1} d\eta \frac{P^m_{i-1}(\eta)P^m_{j-1}(\eta)}{\sqrt{1-\sin(\alpha)\eta}}. \tag{18}$$

$$V^{J\sigma}_{mm}(\alpha) = \frac{1}{4}\frac{J(J+1)-2m^2}{\cos^2(\alpha/2)}, \qquad D^{J\sigma}_{mim\pm1j}(\alpha;R) = \frac{1}{4}\frac{\gamma^{J\sigma}_{mm\pm1}}{\cos^2(\alpha/2)} < mj-1|l_{\mp}|m\pm1j-1> \delta_{ij},$$

$$< mj-1|l_{\mp}|m\pm1j-1 >= [((j-1)\pm1+m)((j-1)\mp m)]^{1/2},$$

$$\gamma^{J\sigma}_{mm+1} = -[1+(\sqrt{2}-1)\delta_{m0}][(J+m+1)(J-m)]^{1/2},$$

$$\gamma^{J\sigma}_{mm-1} = -[1+(\sqrt{2}-1)\delta_{m1}][(J-m+1)(J+m)]^{1/2}.$$

Because of the symmetry of the matrix elements $W_{ij}(\alpha;R)$ with respect to $\alpha=\pi/2$, the problem (13)–(18) will be considered for $\alpha \in [0,\pi/2]$ with the following boundary conditions for the ground and first exited states:

$$\lim_{\alpha\to 0,\pi/2} \sin^2(\alpha)\frac{\partial\boldsymbol{\xi}_m^{(i)}(\alpha;R)}{\partial\alpha} = 0. \tag{19}$$

When $R\to 0$, the zero-order solution $\xi^{(i)}_{jm}(\alpha;R) \equiv \xi_{jmi}(\alpha;R) = \xi^{(0)}_{jmi}(\alpha) + R\xi^{(1)}_{jmi}(\alpha) + ...$ can be presented in the form

$$\xi^{(0)}_{jmi}(\alpha) = \sum_{l_2=|J-(j-1)|}^{J+(j-1)} G^{(j-1)J\sigma}_{ml_2}\phi^K_{(j)l_2}(\alpha)b^i_{l_2l}, \qquad l=j-1, \tag{20}$$

$$G^{(j-1)J\sigma}_{ml_2} = (-1)^{(j-1)+m}\frac{1+\sigma(-1)^{J-(j-1)-l_2}}{[2(1+\delta_{m0})]^{1/2}}C^{l_20}_{j-1mJ-m}, \tag{21}$$

where $C^{l_20}_{lmJ-m}$ are the Clebsch-Gordan coefficients. The functions $\phi^K_{jl_2}(\alpha)$ at $\alpha=2\beta$ are solutions of the eigenvalue problem for the equation

$$T_{ll_2}(\beta)\phi^K_{jl_2}(2\beta) = \frac{1}{4}K(K+4)\phi^K_{jl_2}(2\beta),$$

$$T_{ll_2}(\beta) = \frac{1}{4}\left[-\frac{1}{\sin^2(\beta)\cos^2(\beta)}\frac{\partial}{\partial\beta}\sin^2(\alpha)\cos^2(\beta)\frac{\partial}{\partial\beta} + \frac{l(l+1)}{\sin^2(\beta)} + \frac{l_2(l_2+1)}{\cos^2(\beta)}\right],$$

$$\phi^K_{l'l'_2}(\alpha) = \phi^K_{l'l'_2}(2\beta) = N^K_{ll_2}P^{l+1/2l_2+1/2}_k(cos(2\beta)),$$

$$N^K_{ll_2} = 2^{1/2}\left(\frac{((2k+l+l_2+2)k!(k+l+l_2+1)!}{\Gamma(k+l+3/2)\Gamma(k+l_2+3/2)}\right)^{1/2}, \tag{22}$$

where $\phi^K_{l'l'_2}(2\beta)$ is the normalized Jacobi polynomial, $K=2k+l+l_2$ is hypermomentum and $k=0,1,...$ is the number of nodes of $\phi^K_{l'l'_2}(\alpha)$. Then the zero term of the expansion of the eigenvalue $\varepsilon^{J\sigma}_i(R) \equiv \varepsilon_i(R) = \varepsilon^{(0)}_i + R\varepsilon^{(1)}_i + ...$ is $\varepsilon^{(0)}_i = K(K+4)/4$, while the first correction $\varepsilon^{(1)}_i$, and the zero-order coefficients $b^i_{l'_2l'}$ are

solution of the algebraic eigenvalue problem

$$\sum_{l'=m(\sigma)}^{J+t}\sum_{l'_2=|J-l'|}^{J+l'}\left[W_{ll_2l'l'_2}-\varepsilon_i^{(1)}\delta_{ll'}\delta_{l_2l'_2}\right]b^i_{l'_2l'}=0, \tag{23}$$

$$W_{ll_2l'l_2}=\sum_{m=m(\sigma)}^{J}G^{(j-1)J\sigma}_{ml_2}W_{j-1m(j-1)'m}G^{(j-1)'J\sigma}_{ml'_2},$$

$$W_{mimj}=\int_0^{\pi/2}d\beta\sin^2\beta\cos^2\beta\phi^K_{ll_2}(2\beta)W_{mimj}(2\beta)\phi^K_{l'l'_2}(2\beta). \tag{24}$$

Here $l'_2\le K-l'$, $\quad(-1)^{J-l'_2-l'}=\sigma$, $t=[(K-J)/2]$, i.e., the degeneracy multiplicity (DM) is $DM=(t+1)(J+1)$ for $\sigma=+1, p_t=(-1)^J=(-1)^K$ and $t=[(K-J-1)/2]$, so that $DM=(t+1)(J)$ for $\sigma=-1, p_t=(-1)^{J+1}=(-1)^K$. When two identical electrons 1 and 2 are interchanged, the following relation[7,15] $\sigma(-1)^J(-1)^S=p=\{+1,g(\text{gerade});-1,u(\text{ungerade})\}$ is valid, which connects gerade and ungerade molecular states with the spin $\mathbf{S}=\mathbf{S}_1+\mathbf{S}_2$, at fixed values of the total parity $p_t=\sigma(-1)^J$. This allows one to determine an additional g or u parity of the surface parametric functions.

The 1D weakly singular integral (18) at $\alpha=\pi/2$ can be directly calculated in the analytical form using the Clebsch-Gordan coefficients.[10,31] But this approach gives rise to large numerical errors at large numbers i and j because of the calculation of large-number factorials (the factorials of the numbers up to $4j_{\max}-3$ are required). After the change of the variable in Eq. (18)

$$\eta=\frac{\tan(\alpha/2)}{2}(1-\zeta^2)+\zeta\equiv\eta(\alpha,\zeta),\quad \zeta\in[-1,1],\quad \alpha\in[0,\pi/2], \tag{25}$$

we arrive at the integral having no singularity

$$W^{rep}_{mimj}(\alpha)=W^{rep}_{mimj}(\pi-\alpha)=\frac{1}{\cos(\alpha/2)}\int_{-1}^{1}d\zeta P^m_{i-1+m(\sigma)}\left(\eta(\alpha,\zeta)\right)P^m_{j-1+m(\sigma)}\left(\eta(\alpha,\zeta)\right). \tag{26}$$

The latter 1D integral is calculated using the 96-order GaussianLegendre quadrature, and this approach yields the accuracy $\le 10^{-14}$ at i, $j\le 50$, i.e. the double-precision accuracy.

5. THE INHOMOGENEOUS PARAMETRIC 1D BVP AND THE REDUCED MATRIX ELEMENTS

Taking a derivative of the boundary problem (13)–(15) with respect to the parameter R, we get that $\partial_R\boldsymbol{\xi}^{(i)}(\alpha;R)$ can be obtained as a solution of the following parametric inhomogeneous BVP:

$$\left(\hat{\mathbf{D}}(\alpha;R)-\varepsilon_i(R)\,\hat{\mathbf{I}}\right)\frac{\partial\boldsymbol{\xi}^{(i)}(\alpha;R)}{\partial R}=-\left[\hat{\mathbf{W}}(\alpha)-\frac{\partial\varepsilon_i(R)}{\partial R}\mathbf{I}\right]\boldsymbol{\xi}^{(i)}(\alpha;R), \tag{27}$$

$$\lim_{\alpha\to0}\sin^2(\alpha)\frac{\partial^2\boldsymbol{\xi}^{(i)}(\alpha;R)}{\partial\alpha\partial R}=0,\quad \lim_{\alpha\to\pi}\sin^2(\alpha)\frac{\partial^2\boldsymbol{\xi}^{(i)}(\alpha;R)}{\partial\alpha\partial R}=0. \tag{28}$$

Here $\hat{\mathbf{I}}$, $\hat{\mathbf{D}}(\alpha;R)$ and $\hat{\mathbf{W}}(\alpha)$ are symmetric $[(m(\sigma)+J)j_{\max}]\times[(m(\sigma)+J)j_{\max}]$ matrices:

$$\hat{\mathbf{D}}(\alpha;R)=\{\mathbf{D}_{mm'}(\alpha;R)\}^J_{m,m'=m(\sigma)}=\{\{D_{mjmj'}(\alpha;R)\}^{j_{\max}}_{j,j'=1+m(\sigma)}\}^J_{m,m'=m(\sigma)},$$

$$\hat{\mathbf{W}}(\alpha)=\{\mathbf{W}_{mm}(\alpha)\}^J_{m=m(\sigma)}=\{\{W_{mjmj'}(\alpha)\}^{j_{\max}}_{j,j'=1+m(\sigma)}\}^J_{m=m(\sigma)}.$$

The inhomogeneous parametric BVP (27), (28) has a unique solution if and only if the following conditions are fulfilled

$$\int_0^\pi\sin^2(\alpha)d\alpha\left(\boldsymbol{\xi}^{(i)}(\alpha;R)\right)^T\frac{\partial\boldsymbol{\xi}^{(i)}(\alpha;R)}{\partial R}=0,\quad \frac{\partial\varepsilon_i(R)}{\partial R}=\int_0^\pi\sin^2(\alpha)d\alpha\left(\boldsymbol{\xi}^{(i)}(\alpha;R)\right)^T\mathbf{W}(\alpha)\boldsymbol{\xi}^{(i)}(\alpha;R). \tag{29}$$

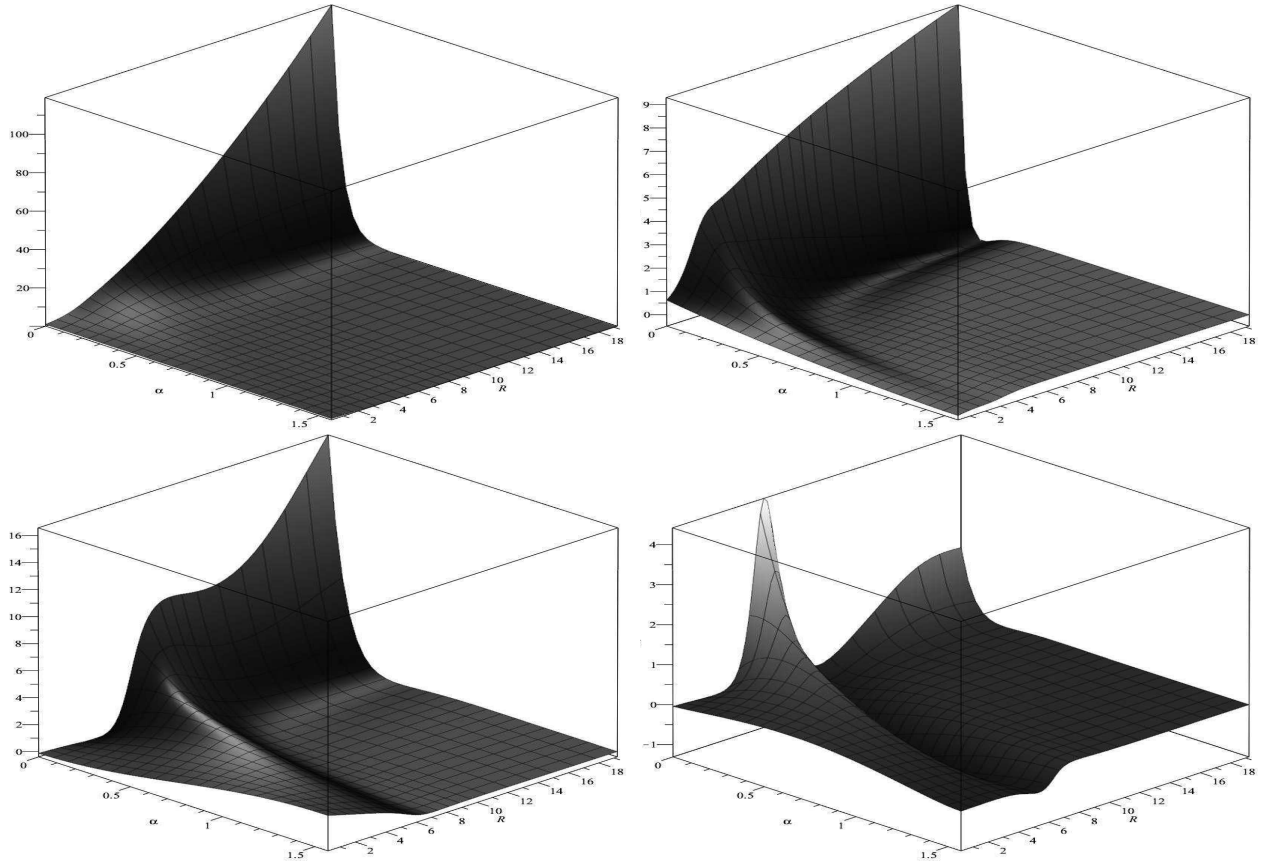

Figure 1. The eigenfunctions $B_{j0}^{J=0\sigma=+1}(\theta,\alpha,R)$ (left) and their first derivatives (right) with respect to the parameter R plotted vs hyperradius R (in a.u.) and the variable α at $\theta=\pi$, $J=0$, $\sigma=+1$. Top: $j=1$. Bottom: $j=4$.

In this case the required matrix elements (8) are reduced to the 1D integrals

$$H_{ij}(R)=H_{ji}(R)=\int_0^\pi \sin^2(\alpha)d\alpha\left(\frac{\partial\boldsymbol{\xi}^{(i)}(\alpha;R)}{\partial R}\right)^T\frac{\partial\boldsymbol{\xi}^{(j)}(\alpha;R)}{\partial R}, \tag{30}$$

$$Q_{ij}(R)=-Q_{ji}(R)=-\int_0^\pi \sin^2(\alpha)d\alpha\left(\boldsymbol{\xi}^{(i)}(\alpha;R)\right)^T\frac{\partial\boldsymbol{\xi}^{(j)}(\alpha;R)}{\partial R}.$$

The homogeneous and inhomogeneous 1D BVPs were solved using the FEM belonging to the Gaussian nodes of a finite-element grid Ω_α at values R on grid Ω_R with the help of the POTHEA program.

Continuity conditions for the eigenfunction $B_{im}^{J\sigma}(\eta,\alpha;R)$. Since the problems (9)–(10) and (13)–(18) are homogeneous, it is necessary to use an additional condition to support the continuity of vector-functions $\boldsymbol{\xi}^{(i)}(\alpha;R)$ and matrix elements (30) with respect to the parameter R in the interval $\Omega_R=[R_{\min},R_{\max}]$. We have used the following procedure:
i) At the first point $R=R_1\in\Omega_R$, we find the value $\alpha=\alpha_0$, for which the eigenfunction $B_{im}^{J\sigma}(\eta_0,\alpha_0;R)$ reaches the absolute maximum value and fix the sign of the eigenfunction $B_{im}^{J\sigma}(\eta_0,\alpha_0;R_1)$. Here $\eta_0\in[\eta_{\min},\eta_{\max}]$ is a fixed point and at least one of the functions $\psi_j(\eta_0)$ in the expansion (11) is nonzero.
ii) At the next points $R\in\Omega_R$ we compute the value of the eigenfunction $B_{im}^{J\sigma}(\eta_0,\alpha_0;R)$ and compare its sign with the previous one. If they are different, we change the sign of $B_{im}^{J\sigma}(\eta_0,\alpha_0;R)$ and again find a new value $\alpha=\alpha_0$, for which the eigenfunction $B_{im}^{J\sigma}(\eta_0,\alpha_0;R_1)$ reaches the absolute maximum value, and again fix the sign of the eigenfunction $B_{im}^{J\sigma}(\eta_0,\alpha_0;R)$.
Note that if the grid Ω_R is sufficiently dense, the above algorithm works well.

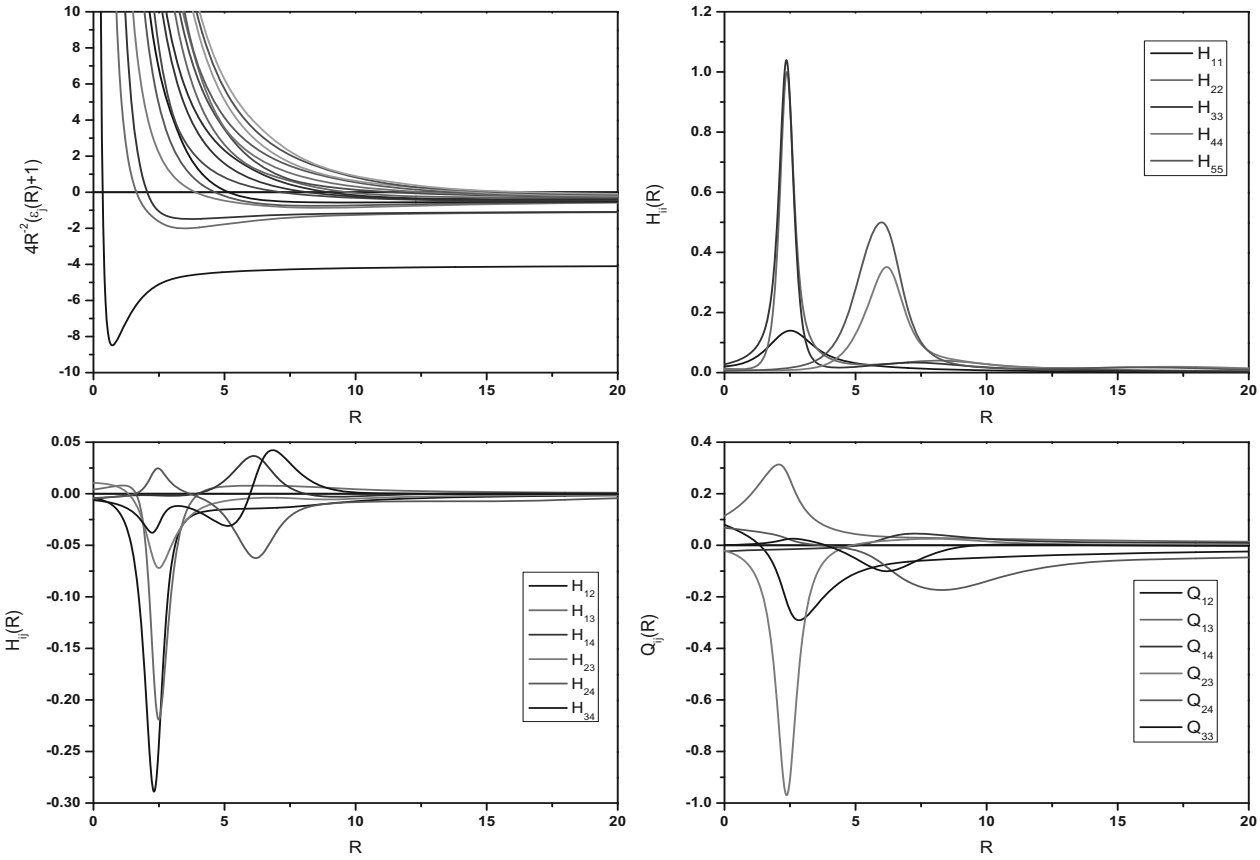

Figure 2. Potential curves $4R^{-2}(\varepsilon_i(R)+1)$ (top-left), diagonal (top-right) and nondiagonal (bottom-left) matrix elements $H_{ij}(R)$, and matrix elements $Q_{ij}(R)$ (bottom-right) plotted vs the hyperradius R (in a.u.) at $J=0$, $\sigma=+1$.

6. RESULTS AND CONVERGENCE OF EXPANSIONS

In Figure 1 the eigenfunctions $B_j(\theta,\alpha,R)$ at $\theta=\pi$ and their first derivatives with respect to parameter R are plotted as functions of the hyperradius R and the variable α at $J=0$ and $\sigma=+1$. The potential curves $4R^{-2}(\varepsilon_i(R)+1)$, the radial diagonal and nondiagonal matrix elements $H_{ij}(R)$, and the radial matrix elements $Q_{ij}(R)$ as functions of the hyperradius R are displayed in Figure 2. As seen from Figures 1 and 2, our continuity condition algorithm for the eigenfunction $B_i(\alpha,\theta;R)$ works well. At small R the DM of the leading terms of potential curves $(\varepsilon_i^{(0)}+1)(4/R^2)=(K+2)^2/R^2$ is determined by the eigenvalues $\varepsilon_i^{(1)}$ of the problem (23). At large R the leading term of potential curves is eigenenergies $(\varepsilon_i^{(0)}+1)(4/R^2)=-4/n^2$ of He^+ ion and the DM is determining by the eigenvalues $\varepsilon_i^{(1)}$ of the dipole integral of motion that are calculated by ASYMPT program.[13] These sets of quantum numbers at small and large R provide complete adiabatic classification of potential curves and corresponding surface functions.[7]

The numerical experiments show strict correspondence with the theoretical estimations for the eigenvalues, eigenfunctions and their derivatives with respect to the parameter.[37] In particular, we calculated the values of the Runge coefficients

$$\beta_l=\log_2\left|\frac{\sigma_l^h-\sigma_l^{h/2}}{\sigma_l^{h/2}-\sigma_l^{h/4}}\right|,\quad l=1\div 6. \tag{31}$$

with absolute errors on four twice condensed grids $\Omega_\alpha^{h=\pi/2/150}=\{0(150)\pi/2\}$ for their eigenvalues, their deriva-

Table 1. Convergence of the potential curves $2R^{-2}(\varepsilon_5(R)+1)$ and the matrix elements $Q_{35}(R)$, $H_{35}(R)$, $H_{55}(R)$ at $R=7.65$ with respect to the maximal number of terms $j_{\max}$, the numbers of finite elements N_{el} at $p=4$, $J=0$, $\sigma=+1$.

$j_{\max}$	N_{el}	$2R^{-2}(\varepsilon_5(R)+1)$	$Q_{35}(R)$	$H_{35}(R),10^{-2}$	$H_{55}(R),10^{-2}$
12	6	–0.371 709 184 126 93	0.134 598 105 140 77	2.269 823 448 3711	8.333 864 894 4523
12	12	–0.371 709 259 032 86	0.134 598 446 320 35	2.269 832 028 2229	8.333 904 465 3504
12	18	–0.371 709 259 378 85	0.134 598 448 023 38	2.269 832 074 7955	8.333 904 678 1835
12	24	–0.371 709 259 392 09	0.134 598 448 089 70	2.269 832 076 6470	8.333 904 686 5992
12	30	–0.371 709 259 393 29	0.134 598 448 095 91	2.269 832 076 8316	8.333 904 687 4409
12	36	–0.371 709 259 393 46	0.134 598 448 097 04	2.269 832 076 8539	8.333 904 687 5470
28	36	–0.371 709 323 600 02	0.134 597 050 762 75	2.270 529 070 0294	8.335 180 574 4351
40	36	–0.371 709 328 860 81	0.134 597 019 884 24	2.270 563 372 5541	8.335 245 600 6930
50	36	–0.371 709 330 261 03	0.134 597 013 520 41	2.270 571 881 3812	8.335 261 797 8755
60	36	–0.371 709 330 888 79	0.134 597 010 970 07	2.270 575 593 4928	8.335 268 874 4977
70	36	–0.371 709 331 210 15	0.134 597 009 749 81	2.270 577 464 9669	8.335 272 444 8158
80	36	–0.371 709 331 391 12	0.134 597 009 092 13	2.270 578 508 8896	8.335 274 437 1520
100	36	–0.371 709 331 570 62	0.134 597 008 464 54	2.270 579 535 9914	8.335 276 397 9589
120	36	–0.371 709 331 649 80	0.134 597 008 196 86	2.270 579 986 5607	8.335 277 258 2599

Table 2. Convergence of the potential curves $2R^{-2}(\varepsilon_{45}(R)+1)$ and the matrix elements $Q_{4345}(R)$, $H_{4345}(R)$, $H_{4545}(R)$ at $R=7.65$ with respect to the maximal number of terms $j_{\max}$, the numbers of finite elements N_{el} at $p=4$, $J=0$, $\sigma=+1$.

$j_{\max}$	N_{el}	$2R^{-2}(\varepsilon_{45}(R)+1)$	$Q_{4345}(R),10^{-3}$	$H_{4345}(R),10^{-4}$	$H_{4545}(R),10^{-3}$
28	6	4.879 922 636 3814	7.163 551 693 5081	1.313 245 172 8746	1.034 074 714 0100
28	12	4.878 939 387 2213	7.192 416 552 7016	1.313 393 326 9761	1.037 535 372 8940
28	18	4.878 936 678 0110	7.192 470 461 7592	1.313 394 061 3732	1.037 544 063 9450
28	24	4.878 936 575 2142	7.192 471 802 1313	1.313 393 807 6831	1.037 544 380 3934
28	30	4.878 936 565 5674	7.192 471 876 6182	1.313 393 761 6265	1.037 544 409 1011
28	36	4.878 936 564 0653	7.192 471 882 3076	1.313 393 751 7463	1.037 544 413 4573
40	36	4.878 929 789 5129	7.164 925 249 6742	1.304 767 510 9540	1.036 946 196 5037
50	36	4.878 928 117 4560	7.158 600 336 8535	1.302 825 852 3511	1.036 806 107 8060
60	36	4.878 927 388 1689	7.155 920 393 0868	1.302 012 009 2210	1.036 746 299 2434
70	36	4.878 927 020 3953	7.154 591 453 2935	1.301 611 523 1378	1.036 716 518 7633
80	36	4.878 926 815 1861	7.153 857 856 1010	1.301 391 714 3581	1.036 700 039 4171
100	36	4.878 926 613 2176	7.153 142 578 7764	1.301 178 645 2747	1.036 683 940 9568
120	36	4.878 926 524 5981	7.152 831 407 8959	1.301 086 493 8366	1.036 676 926 5296

tives, and matrix elements, respectively:

$$\sigma_1^h=|\varepsilon_j^{h/8}(\rho)-\varepsilon_j^h|,\quad \sigma_2^h=\left|\frac{\partial\varepsilon_j^{h/8}(R)}{\partial R}-\frac{\partial\varepsilon_j^h}{\partial R}\right|$$
$$\sigma_3^h=\|\boldsymbol{\xi}_j^{h/8}(\alpha;R)-\boldsymbol{\xi}_j^h(\alpha;R)\|_0,\quad \sigma_4^h=\left\|\frac{\partial\boldsymbol{\xi}_j^{h/8}(\alpha;R)}{\partial R}-\frac{\partial\boldsymbol{\xi}_j^h(\alpha;R)}{\partial R}\right\|_0, \tag{32}$$
$$\sigma_5^h=|H_{1j}^{h/8}(R)-H_{1j}^h(R)|,\quad \sigma_6^h=|Q_{1j}^{h/8}(R)-Q_{1j}^h(R)|,$$

From (31) we obtained numerical estimations of the convergence order of proposed numerical schemes, i.e., the theoretical estimations equal to $\beta_l=p+1$ for $l=3,4$ and $\beta_l=2p$ otherwise. For the chosen approximation order $p=4$ for their eigenvalues, derivatives, and matrix elements we obtained numerical estimations of the Runge coefficients within $7.5\div7.8$, and for their eigenfunctions and their derivatives in the range $4.6\div4.8$, which corresponds to the theoretical error estimates at fixed number j_{max} of equations (13). The calculations (32) were performed with specified accuracy of $\sim10^{-12}$ by means of POTHEA program at relative error tolerance

Table 3. Convergence of the ground state energy (in a.u.) for a helium atom versus the number N of basis functions and the number $j_{\max}$ of the Legendre polynomials at $J = 0$, $\sigma = +1$.

N	$j_{\max} = 12^{12}$	$j_{\max} = 12$	$j_{\max} = 21$	$j_{\max} = 28$	$j_{\max} = 40$	$j_{\max} = 50$
1	−2.887 911 68	−2.895 539 19	−2.895 551 19	−2.895 552 76	−2.895 553 52	−2.895 553 71
2	−2.891 379 91	−2.898 631 57	−2.898 643 21	−2.898 644 74	−2.898 645 47	−2.898 645 66
6	−2.903 004 48	−2.903 644 06	−2.903 655 96	−2.903 657 52	−2.903 658 27	−2.903 658 46
10	−2.903 636 13	−2.903 702 86	−2.903 714 79	−2.903 716 36	−2.903 717 10	−2.903 717 30
15	−2.903 705 49	−2.903 708 67	−2.903 720 60	−2.903 722 16	−2.903 722 91	−2.903 723 10
21	−2.903 722 64			−2.903 722 99	−2.903 723 74	−2.903 723 93
28	−2.903 722 66				−2.903 723 74	−2.903 723 93
35					−2.903 723 91	−2.903 724 10
40						−2.903 724 10
45						−2.903 724 15
10						−2.903 722 99
17						−2.903 724 37

Table 4. Convergence of the first exited state energy (in a.u.) of a helium atom versus the number N of basis functions and the number $j_{\max}$ of the Legendre polynomials at $J = 0$, $\sigma = +1$.

N	$j_{\max} = 12$	$j_{\max} = 21$	$j_{\max} = 28$	$j_{\max} = 35$	$j_{\max} = 40$	$j_{\max} = 50$
1	−2.139 934 95	−2.139 935 59	−2.139 935 68	−2.139 935 71	−2.139 935 72	−2.139 935 73
2	−2.141 663 86	−2.141 664 27	−2.141 664 32	−2.141 664 34	−2.141 664 35	−2.141 664 36
6	−2.145 699 44	−2.145 700 08	−2.145 700 17	−2.145 700 20	−2.145 700 21	−2.145 700 22
10	−2.145 914 25	−2.145 914 95	−2.145 915 04	−2.145 915 07	−2.145 915 09	−2.145 915 10
15	−2.145 956 50	−2.145 957 21	−2.145 957 30	−2.145 957 34	−2.145 957 35	−2.145 957 36
21			−2.145 968 71	−2.145 968 74	−2.145 968 76	−2.145 968 77
28				−2.145 970 24	−2.145 970 26	−2.145 970 27
35					−2.145 972 10	−2.145 972 11
40						−2.145 972 63
45						−2.145 973 22
10						−2.145 956 97
18						−2.145 974 04

$\epsilon_1 = 4 \cdot 10^{-16}$ of the calculated eigenvalues (13) using the computer 2 x Xeon 3.2 GHz, 4 GB RAM with Intel Fortran 77 and the data type of real*8, which provides 16 significant digits. The running time for this example is 2 seconds for $j_{\max} = 12$, $N = 6$ and 1000 seconds for $j_{\max} = 50$, $N = 50$.

The results of the convergence study for several matrix elements with respect to the number $j_{\max}$ =12, 28, 40, 50, 60, 70, 80, 100, 120 of the Legendre polynomials and the number of finite elements, $N_{el} = 6$, 12, 18, 24, 30, 36, of the grid $\Omega_\alpha = \{0(N_{el})\pi/2\}$ and their order $p = 4$ are presented in Tables 1 and in 2. One can see that the potential curves $2R^{-2}(\varepsilon_j(R) + 1)$ and the matrix elements $H_{ij}(R)$ converge monotonically from above, with the increasing numbers N_{el} and $j_{\max}$. The absolute values of the matrix elements $Q_{ij}(R)$ converge monotonically from above with increasing $j_{\max}$ and from below with increasing N_{el}.

As shown in Table 1, the convergence of eigenvalues and matrix elements vs the number of Legendre polynomials $P_{j-1}(\eta)$, is proportional to their order $\sim j^{-3}$. It follows from the estimations of the matrix elements $W_{i \ll j}(\alpha) \sim 1/\sqrt{j}$ (in particular, for the integral (18) at $i = 1$, we have $W^{rep}_{1j}(\alpha) = \sqrt{2}\exp(-(j - 1/2)\mathrm{arch}(\sin^{-1}\alpha))/(\sqrt{2j-1}\sqrt{\sin\alpha}$, $\alpha > 0$, see, for example,[44]) and $\lambda_{j-1} = (j-1)j \sim j^2$, which leads to the estimations for the correction of eigenvalues $\delta\varepsilon \sim j^{-3}$ within the second-order perturbation theory.

In the benchmark calculations the grids in R and α have been chosen as follows: $\Omega_R = \{0(200)10(200)30\}$ and $\Omega_\alpha = \{0(150)\pi/2\}$. Enclosed in parentheses are the numbers of finite elements of the order $p = 4$ in each interval. The set of matrix elements including the eigenfunction with number $N = 50$ were calculated with an accuracy of an order of 10^{-8}, using the number of finite elements $N_{el} = 150$ at $\epsilon_2 = 10^{-12}$. The banded system of (150*4+1)*50=30050 linear algebraic equations corresponding to the BVP (13)–(18) with the mean bandwidth (4+1)*50=250 has been stably solved with the relative error tolerance $\epsilon_2 = 10^{-12}$ at each value of hyperradius

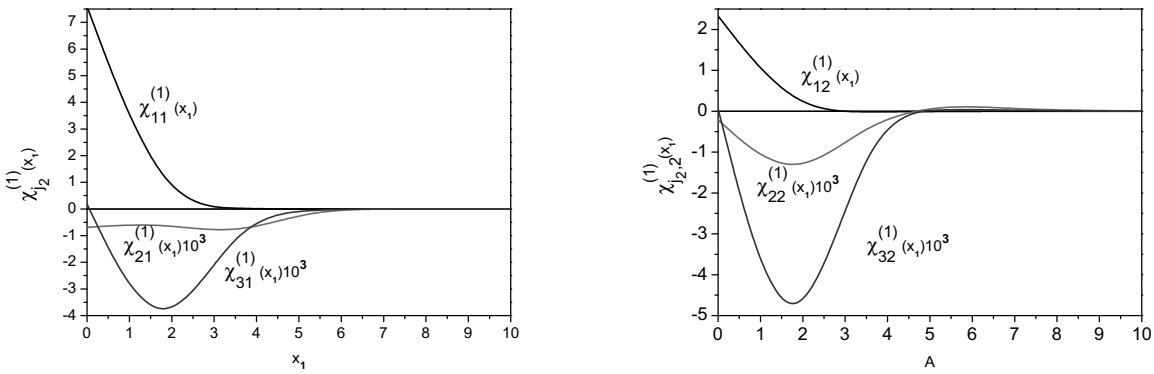

Figure 3. Components of radial vector-eigenfunctions vs R (in a.u.) of ground and first exited states $^1S^e$ of He atom.

R belonging to the set of Gaussian nodes of the grid Ω_R. The results of the convergence study of the ground and first exited state energies of a Helium atom calculated by means of KANTBP program with the number N of radial equations (6) and the number $j_{\max}$ of the Legendre polynomials are presented in Tables 3 and 4, and the corresponding radial functions are presented in Fig. 3. One can see that the energy eigenvalues converge monotonically from above, with the $N = 45$, $j_{\max} = 50$ – channel value being $E_1 = -2.903\,724\,15$ a.u. and $E_2 = -2.145\,973\,22$ a.u., as well as maxima of absolute values of components of radial vector-functions in Fig. 3.

Tables show that the obtained results agree with the accuracy of the order of 10^{-6} at $j_{\max} \sim N$ with variational estimations[17,18] and have higher accuracy than the previous coupled-channel hyperspherical adiabatic calculations.[10,12]

7. CONCLUSION

The boundary value problem (BVP) for the system of coupled self-adjoined 3D elliptic partial differential equations of the Schrödinger type with homogeneous boundary conditions aimed for studying the models of two-electron composite quantum systems like a Helium atom in hyperspherical coordinates was formulated within the coupled-channel adiabatic approach. The numerical analysis proved that the finite-element discretization of the problem and the developed numerical schemes and algorithms implemented in Fortran 77, as well as the program complex POTHEA, provide stable calculations with the specified accuracy of $\sim 10^{-12}$ of the parametric eigenfunctions and their derivatives with respect to the parameter within an accuracy of the same order $O(h^{p+1})$, as well as its parameter eigenvalues, their derivatives and the matrix elements within an accuracy of the same order $O(h^{2p})$ in step h of the finite element grid, in accordance with theoretical estimations at fixed number j_{max} of equations (13), i.e. the homogeneous and nonhomogeneous parametric 1D BVPs. Numerical analysis proved that convergence of eigenvalues and matrix elements vs the number j_{max} of Legendre polynomials of the expansion (13) is proportional to the inverse cube of their order in accordance with theoretical estimations. The benchmark calculations with required accuracy of order of $\sim 10^{-8}$ of the matrix elements and of order of $\sim 10^{-6}$ of eigenenergies of ground and first exited states of a helium atom confirm the applicability of the elaborated algorithms and program packages POTHEA and KANTBP at reasonable computer resource ($j_{max} \sim N \sim 50$) and have higher accuracy than the previous coupled-channel hyperspherical adiabatic calculations.[10,12] Thus, a similar accuracy can be achieved also in calculations of high exited states of the He atom or multichannel scattering states $e + H$ in uniform magnetic field, for which the variational calculations were not usually applied, taking into account the appropriate asymptotic behavior of the matrix elements and solutions .[10]

The elaborated method, algorithms and programs for calculation of parametric eigenvalues, eigenfunctions (parametric basis functions) and the matrix elements can be used for the numerical solution with the required accuracy of the bound-state and scattering problems with the system of the coupled three-dimensional equations of the Schrödinger type, including short-range and long-range potentials of the Coulomb type,[45,46] or for various

system of the coupled three-dimensional elliptic equations in partial derivatives(PDEs), with the help of the proposed program complexes. The generalization of the algorithm for solving a system of the parametric coupled BVP for 2D PDEs in the framework of the projection method and FEM, which can be applied for solving multidimensional boundary value problems for equations of Schrödinger type, describing models of composite quantum systems like photoionization of negative hydrogen ion in uniform magnetic field, photoabsorption in two electron or exciton states in quantum dots, will be presented in further papers.

7.1 Acknowledgments

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