Adiabatic representation for the three-body problem in the limit of separated atoms in appropriate coordinates

M. B. Kadomtsev
I. V. Kurchatov Institute of Atomic Energy, 123 182 Moscow, U.S.S.R.

S. I. Vinitsky
Laboratory of Theoretical Physics, Joint Institute for Nuclear Research, Dubna, Head Post Office, Post Office Box 79, 101 000 Moscow, U.S.S.R.

F. R. Vukajlović
Laboratory for Theoretical Physics (020), The Boris Kidrić Institute for Nuclear Sciences, Vinča, Post Office Box 522, YU-11001 Belgrade, Yugoslavia
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An equivalent operator $\tilde{\Lambda}$ removing the Coulomb degeneracy in the second order of perturbation theory for the two-center problem in the limit of separated atoms is found. Eigenvalues and eigenfunctions of the operator $\tilde{\Lambda}$ allow us to construct a complete classification of states of the two-center problem in appropriate coordinates, a compatible adiabatic basis (CAB). Averaging of the total Hamiltonian of a three-body problem over CAB results in a system of adiabatic equations in slow variable $\mathcal{R}$, the hyperradius of the three-body problem. It is shown that asymptotics of that system of equations is compatible with physical boundary conditions of the scattering problem.

I. INTRODUCTION

The adiabatic representation of the three-body problem is widely used in the physics of atomic collisions and it is well known in literature as a method of the perturbed stationary state (PSS).[1] Recently this method has been further developed in connection with problems of mesoatomic physics related to the muon catalysis of nuclear fusion.[2] Let us note that a total set of solutions of the two-center problem of quantum mechanics has been mostly used as an adiabatic basis.[3] This is due to the fact that the variables of the two-center problem could be separated and effective numerical algorithms were developed for its solution. Replacement of an electron with a more massive muon, in problems of mesoatomic physics, increased the role of the nonadiabatic connection between channels. This resulted in the necessity to take into account about 1000 basis functions for the precise calculations of weakly bound $dd\mu$ and $dt\mu$ mesomolecular states.[4] The existence of a great number of basis functions made possible the correct formulation of boundary conditions in the adiabatic representation, which were in agreement with physical boundary conditions of the scattering problem.[5] The calculated cross sections for low-energy scattering of muonic atoms in the mixture of hydrogen isotopes showed the reliability and accuracy of this approach.[6]

Regardless of the definite successes of the standard adiabatic method, the discussions about the weakening of the nonadiabatic connection between channels have been going on for a long period of time. The main goal of all attempts has been the formation of more economical adiabatic basis, asymptotically compatible with physical boundary conditions of the scattering problem.[7] For atomic systems of the H^-, He, etc., type, the hyperspherical adiabatic basis was suggested.[8] The development of a molecular hyperspherical approach for mesomolecular systems was given in Refs. 9 and 10. As was shown in those papers, the main problem, which had to be solved in order to get a compatible adiabatic basis (CAB), was to find suitable coordinates $\mathcal{R},\mathbf{r}'$. These coordinates, in each of reaction channels, asymptotically transform into appropriate pairs of Jacobi coordinates (Fig. 1). Then, in the case of slow collisions, the relative motion of the mesoatom and nucleus in a $[(ac)+b]$ and b $[a+(bc)]$ channels is described by the exact reduced mass. In that case the CAB transforms into wave functions of separated atoms. However, in such an approach, one must solve numerically the two-center problem with unseparated variables. In recent papers,[11,12] a hyperspherical adiabatic basis was already used for the

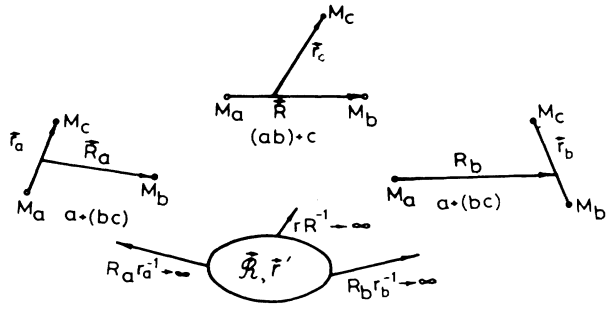

FIG. 1. Jacobi coordinate systems for three particles (abc).

calculation of energy levels of $Ps^- \equiv e^+e^-e^-$ and HD^+. Standard methods have been used, which do not allow the calculation of highly excited states of the two-center problem.

Our starting point in this work is that effective numerical algorithms for the solution of many-dimensional problems are known.[13] Then, it is necessary to find the classifications of CAB states and the asymptotics of the solutions of adiabatic equations in the limit of separated atoms. In our earlier paper,[10] this problem was solved for the case of zero total angular momentum of the three-body system. Here we are looking for the classification of CAB in the case of nonzero total angular momentum. It is shown that in the limit of separated atoms, states of CAB can be classified by the eigenvalues of operator $\tilde{\Lambda}$. If we take into account adiabatic corrections, this operator turns into the well-known dipole constant of motion Λ for the scattering of an atom on a charged particle.[14] The muonic angular momentum in the limit of separated atoms $(\alpha c), \alpha = a, b$ is quantized on the Z_α axis, which is directed along the Jacobi vector $\mathbf{R}_\alpha$. This vector connects a distant charged particle with the atomic center of mass (Figs. 1 and 2). Let us note that in the standard adiabatic basis such a "requantization" of muonic angular momentum from molecular axis Z to Z_α can be done only after the nonadiabatic connection is taken into account[5] (cf. Fig. 2).

In the adiabatic system of equations depending on the slow variable $\mathcal{R}$, which was obtained by means of averaging the total Hamiltonian over CAB, strong nonadiabatic coupling in channels α does not exist. Such strong coupling is the characteristic feature of the standard adiabatic approach.[5,7]

Some residual nonadiabatic weak coupling is proportional to $\mathcal{R}^{-1}\partial/\partial\mathcal{R}$ and its origin is in the difference between the magnitudes of hyperradius $\mathcal{R}$ and Jacobi vector $\mathbf{R}_\alpha$. This difference is of order $O(\mathcal{R}^{-1})$. It has been shown that the inclusion of this weak coupling, for large finite $\mathcal{R}$, establishes the magnitude of the Jacobi vector $\mathbf{R}_\alpha$ in the asymptotics of the component ψ_α of the total wave function $\psi = \psi_a + \psi_b$, so that ψ is in agreement with physical boundary conditions of the scattering problem.

The connection between adiabatic asymptotic expressions and the well-known expression for the scattering amplitude of charged-particle scattering on atoms in dipole approximation[15] was also established. In that case the phase shift from the dipole potential is separated explicitly in accordance with quantum-defect theory.[16,17]

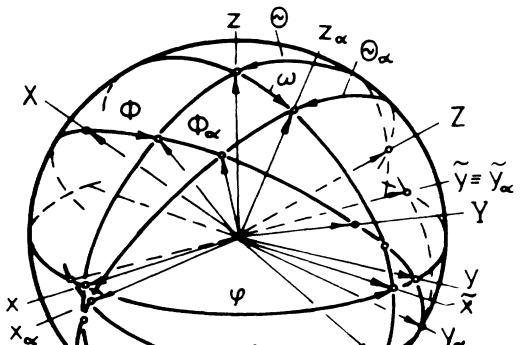

FIG. 2. Rotating coordinate systems xyz and $x_\alpha y_\alpha z_\alpha$ are defined on spherical unit vectors of Jacobi vectors $\mathbf{R} = \{R\Theta\Phi\}$ and $\mathbf{R}_\alpha = \{R_\alpha\Theta_\alpha\Phi_\alpha\}$. The following relations between angles $\Theta_\alpha\Phi_\alpha\varphi_\alpha$ and $\Theta\Phi\varphi$ are valid (Ref. 18): $\cos\Theta_\alpha = \cos\Theta\cos\omega + \sin\Theta\sin\omega\cos(\pi-\varphi)$; $\cot(\Phi_\alpha - \Phi) = \cos\Theta\cot\varphi + \cot\omega(\sin\Theta/\sin\varphi)$; $\cot\phi_\alpha = \cos\omega\cot\phi + \cot\Theta(\sin\Theta/\sin\phi)$, where φ_α and φ are rotation angles about the z_α and z axes.

II. STATEMENT OF THE PROBLEM

A. Hamiltonian

Let us examine the system of three Coulomb particles a, b, and c with charges Z_a, Z_b, and $Z_c = -1$ and masses M_a, M_b, and M_c $(e = \hbar = 1)$. Further, we shall suggest that particles a and b are nuclei while particle c is a muon and that $M_a \geq M_b > M_c$. In accordance with the Ref. 9, suitable variables $\mathcal{R}, \mathbf{r}'$ can be introduced, which are connected with the standard Jacobi coordinates $\mathbf{r}_c, \mathbf{R}$ (Fig. 1) by the following relations:

$$\begin{aligned} &\mathbf{r}' = D(\Theta,\Phi)\mathbf{r}_c/R, \quad \mathcal{R} = \mathcal{R}\mathbf{e}_R , \\ &\mathcal{R} = [R^2 + (m/M)r_c^2]^{1/2} = \sqrt{\rho}R , \end{aligned} \tag{1}$$

where

$$m^{-1} = (M_a + M_b)^{-1} + M_c^{-1}, \quad M^{-1} = M_a^{-1} + M_b^{-1} .$$

The components of $\mathbf{r}'$ and $\mathcal{R}$ are determined in the rotating coordinate system with Z axis directed along $\mathbf{R} = R\mathbf{e}_R$. Axes x and y are directed along spherical unit vectors $\mathbf{e}_\Theta$ and $\mathbf{e}_\Phi$ (Fig. 2). Rotation matrix $D(\Theta,\Phi)$ performs the transition from fixed XYZ into the rotating coordinate system xyz and differs from the standard one only by cyclic permutation of rows.[18] The Schrödinger equation in suitable variables (1) has the form

$$\begin{aligned} &H\psi = E\psi, \quad H = -\frac{1}{2M}\frac{1}{\mathcal{R}^5}\frac{\partial}{\partial\mathcal{R}}\mathcal{R}^5\frac{\partial}{\partial\mathcal{R}} + h , \\ &h = -\frac{1}{2m}\frac{\rho^2}{\mathcal{R}^2}\Delta_{\mathbf{r}'} + \frac{1}{M}\frac{\rho}{\mathcal{R}^2}\mathbf{r}'\cdot\nabla_{\mathbf{r}'} + V + \rho\frac{\mathbf{J}^2 - 2\mathcal{L}\cdot\mathbf{J}}{2M\mathcal{R}^2} . \end{aligned} \tag{2}$$

Here h is the Hamiltonian of the two-center problem in the total angular momentum $\mathbf{J} = \mathcal{L} + \mathbf{L}$ representation; $\mathcal{L} = -i[\mathbf{r}'\nabla_{\mathbf{r}'}]$ is muon angular momentum with respect to the center of mass of the nuclei;

$$\begin{aligned} L = \mathbf{e}_\Theta[(i/\sin\Theta)\partial/\partial\Phi - \mathcal{L}_x + \cot\Theta\mathcal{L}_z] \\ + \mathbf{e}_\Phi(i\partial/\partial\Theta - \mathcal{L}_y) \end{aligned}$$

is angular momentum of relative motion of nuclei;

$$2\mathcal{L}\cdot\mathbf{J} = \mathcal{L}_+J_- + \mathcal{L}_-J_+ + 2J_z^2$$

is the operator of Coriolis interaction; $J_z = \mathcal{L}_z$,

$$\mathcal{L}_{\pm}:=\mathbf{e}_{\pm}\cdot\mathcal{L}=\mathcal{L}_x\pm i\mathcal{L}_y,\quad \mathbf{e}_{\pm}=\mathbf{e}_{\Theta}\pm i\mathbf{e}_{\Phi}\ ,$$

$$J_{\pm}:=\mathbf{e}_{\pm}\cdot\mathbf{J}=J_x\pm iJ_y$$
$$=\pm\partial/\partial\Theta+(i/\sin\Theta)\partial/\partial\Phi+\cot\Theta\mathcal{L}_z$$

are spherical components of $\mathcal{L}$ and $\mathbf{J}$. Operators $\mathcal{L}^2$ and $\mathbf{J}^2$ are expressed through these components with the relations

$$\mathcal{L}^2=\tfrac{1}{2}(\mathcal{L}_+\mathcal{L}_-+\mathcal{L}_-\mathcal{L}_+)+\mathcal{L}_z^2\ ,$$

$$\mathbf{J}^2=\tfrac{1}{2}(J_+J_-+J_-J_+)+\tfrac{1}{2}\cot\Theta(J_--J_+)+J_z^2\ .$$

[Here operators $J_{\pm}$ differ from standard raising $\tilde{J}_-$ and lowering $\tilde{J}_+$ ones: $\tilde{J}_{\pm}=e^{\mp i\varphi}J_{\pm}$. The latter are defined on the unit vectors $\tilde{\mathbf{e}}_{\pm}=e^{\mp i\varphi}\mathbf{e}_{\pm}$: $\tilde{J}_{\pm}=\tilde{\mathbf{e}}_{\pm}\cdot\mathbf{J}$ in the coordinate system $\tilde{x}\tilde{y}z$, which is obtained from xyz by a rotation of angle φ about the z axis (Fig. 2). Then the operator $\mathbf{J}^2$ is given by the well-known formula $\mathbf{J}^2=\frac{1}{2}(J_+J_-+J_-J_+)+J_z^2$.] Coulomb potential energy V and the volume element $d\tau$ are given by

$$V=-\frac{\sqrt{\rho}}{\mathcal{R}}\left[\frac{Z_a}{|\mathbf{r}'+\gamma_a\mathbf{e}_R|}+\frac{Z_b}{|\mathbf{r}'-\gamma_b\mathbf{e}_R|}-Z_aZ_b\right],$$

$$\gamma_a+\gamma_b=1,\quad \gamma_a=M_b/(M_a+M_b),\ \gamma_b=M_a/(M_a+M_b)\ ,$$

$$d\tau=\mathcal{R}^5\,d\mathcal{R}\,\rho^{-3}d\mathbf{r}'\sin\Theta\,d\Theta\,d\Phi,\quad \rho=1+(m/M)(r')^2\ .$$

B. Compatible adiabatic basis

Let us take as the adiabatic basis a complete set of the solutions of the two-center problem (CAB)

$$h\phi_i(\Omega;\mathcal{R})=E_i(\mathcal{R})\phi_i(\Omega;\mathcal{R}) \tag{3}$$

defined in the region $\Omega=\{\mathbf{r}'\Theta\Phi\}$ with the volume element

$$d\Omega=\mathcal{R}^3\rho^{-3}\,d\mathbf{r}'\sin\Theta\,d\Theta\,d\Phi$$

and the normalization condition

$$\langle\phi_i\,|\,\phi_j\rangle=\int d\Omega\,\phi_i^*(\Omega;\mathcal{R})\phi_j(\Omega;\mathcal{R})=\delta_{ij}\ . \tag{4}$$

Here the terms $E_i(\mathcal{R})$ are eigenvalues of the two-center problem depending parametrically on the collective variable $\mathcal{R}$; $\{i\}$ is the set of quantum numbers. Due to the small parameter $m/M<1$ in the Hamiltonian (2), the motion in the region Ω can be regarded as fast when compared with the motion over $\mathcal{R}$. This parameter for the mesomolecular systems is ~ 0.1. Therefore, terms $E_i(R)$ can be treated as effective potentials in which a slow collective motion of the three-body system occurs. The existence of two attractive potentials in h leads to the solutions of Eq. (3), which turn into wave functions of separated atoms localized near charges Z_a and Z_b in the limit of $\mathcal{R}\to\infty$. In that way, asymptotic classification of these solutions can be given and the total wave function expressed as a sum

$$\Psi(\Omega,\mathcal{R})=\Psi_a(\Omega,\mathcal{R})+\Psi_b(\Omega,\mathcal{R})\ , \tag{5}$$

where

$$\Psi_\alpha(\Omega,\mathcal{R})=\sum_i\phi_{i\alpha}(\Omega;\mathcal{R})\mathcal{R}^{-1}\chi_{i\alpha}(\mathcal{R})\ .$$

Index $\alpha=a,b$ is explicitly extracted from the set $\{i\}$ so that the orthogonality condition (4) now has the form

$$\langle\phi_{i\alpha}\,|\,\phi_{j\beta}\rangle=\delta_{ij}\delta_{\alpha\beta}=I\delta_{\alpha\beta}=\langle\phi_\alpha\,|\,\phi_\beta\rangle\ . \tag{4'}$$

For identical nuclei, additional degeneracy appears as a result of symmetry of the Hamiltonian h under the permutation of nuclei P_n. In that case, solutions $\phi_\alpha\equiv\{\phi_{i\alpha}\}$ are connected with g (even) and u (odd) solutions of Eq. (3) by following standard relations:

$$\begin{aligned}\phi_{ia}&=(1/\sqrt{2})(\phi_{ig}-\phi_{iu})\ ,\\ \phi_{ib}&=(1/\sqrt{2})(\phi_{ig}+\phi_{iu})\ .\end{aligned} \tag{6}$$

C. Radial equations

In order to get an adiabatic system of equations over the slow variable $\mathcal{R}$ it is necessary to average Eq. (2) over the two-center functions $\phi_{i\alpha}(\Omega;\mathcal{R})$. This procedure can be simplified if we transform wave function Ψ to $\tilde{\Psi}=\rho^{3/2}\mathcal{R}\Psi$. Then total Hamiltonian takes the form

$$\tilde{H}=\mathcal{R}\rho^{3/2}H\rho^{-3/2}\mathcal{R}^{-1}$$
$$=-\frac{1}{2M}\left[\frac{\partial^2}{\partial\mathcal{R}^{2+}}\frac{3}{\mathcal{R}}\frac{\partial}{\partial\mathcal{R}}\right]+\frac{3}{2M\mathcal{R}^2}+\tilde{h}\ ,$$

$$\tilde{h}=\rho^{3/2}h\rho^{-3/2}=-\frac{1}{2m}\frac{\rho^2}{\mathcal{R}^2}\Delta_{\mathbf{r}'}+\frac{2}{M}\frac{\rho}{\mathcal{R}^2}Q^{(0)}+V$$
$$+\rho\frac{\mathbf{J}^2-2\mathcal{L}\cdot\mathbf{J}}{2M\mathcal{R}^2}-\frac{3}{2M\mathcal{R}^2}\ , \tag{7}$$

$$Q^{(0)}=-(3/2+\mathbf{r}'\cdot\nabla\mathbf{r}')\ .$$

Eigenfunctions $\tilde{\phi}_{i\alpha}(\Omega;\mathcal{R})$ of the Hamiltonian $\tilde{h}$ are normalized by the condition (4') with simpler volume element

$$d\tilde{\Omega}=\mathcal{R}^3\,d\mathbf{r}'\sin\Theta\,d\Theta\,d\Phi\ ,$$

while the total volume element is equal to $d\tilde{\tau}=d\mathcal{R}\,d\tilde{\Omega}$. The adiabatic system of equations for the vector of solutions $\chi_\alpha\equiv\{\chi_{i\alpha}\}$ becomes

$$\left[I\frac{d^2}{d\mathcal{R}^2}+2ME-V_{\alpha\alpha}\right]\chi_\alpha=\sum_{\beta(\neq\alpha)}V_{\alpha\beta}\chi_\beta\ , \tag{8}$$

where

$$V_{\alpha\beta}=2Q_{\alpha\beta}\frac{d}{d\mathcal{R}}+K_{\alpha\beta}+2M\left[E_\alpha(R)+\frac{4}{2M\mathcal{R}^2}\right]\delta_{\alpha\beta}I\ ,$$

$$Q_{\alpha\beta}=-\frac{3}{2}\frac{1}{\mathcal{R}}\delta_{\alpha\beta}I-\left\langle\tilde{\phi}_\alpha\left|\frac{\partial}{\partial\mathcal{R}}\right|\tilde{\phi}_\beta\right\rangle\ ,$$

$$K_{\alpha\beta}=-\frac{1}{\mathcal{R}^2}-\left\langle\tilde{\phi}_\alpha\left|\frac{\partial^2}{\partial\mathcal{R}^2}+\frac{3}{\mathcal{R}}\frac{\partial}{\partial\mathcal{R}}\right|\tilde{\phi}_\beta\right\rangle\ .$$

D. Asymptotic form of radial equations

If we pass from $\mathbf{r}'$ to $\mathbf{r}=\mathbf{r}'\cdot\mathcal{R}$ in the asymptotic region $\mathcal{R}\to\infty$, then the asymptotic two-center Hamiltonian

$$\tilde{h}_{as}=-\frac{1}{2m}\rho^2\Delta_{\mathbf{r}}+\frac{2}{M}\frac{\rho}{\mathcal{R}^2}Q^{(0)}+V+\rho\frac{J^2-2\mathcal{L}\cdot\mathbf{J}}{2M\mathcal{R}^2}-\frac{3}{2M\mathcal{R}^2}\ , \tag{9}$$

with an accuracy of $O(\mathcal{R}^{-1})$, transforms to the Hamiltonian of separated atoms (ac) and (bc).[10] After the same transformation, matrix elements in the adiabatic system of equations become

$$Q_{\alpha\beta}=\mathcal{R}^{-1}Q^{(0)}_{\alpha\beta}+\left\langle\tilde{\phi}_\alpha\left|-\frac{\partial}{\partial\mathcal{R}}\right|\tilde{\phi}_\beta\right\rangle\ ,$$

$$K_{\alpha\beta}=\mathcal{R}^{-2}K^{(0)}_{\alpha\beta}+\left\langle\tilde{\phi}_\alpha\left|-\frac{\partial^2}{\partial\mathcal{R}^2}+2Q^{(0)}\frac{1}{\mathcal{R}}\frac{\partial}{\partial\mathcal{R}}\right|\tilde{\phi}_\beta\right\rangle\ ,$$

$$K^{(0)}=-1-[(\mathbf{r}\cdot\nabla_{\mathbf{r}})^2+2(\mathbf{r}\cdot\nabla_{\mathbf{r}})]\ .$$

Here scalar product (4′) is defined with volume element $d\tilde{\Omega}_{as}=d\mathbf{r}\sin\Theta\,d\Theta\,d\Phi$. In the limit of $\mathcal{R}\to\infty$ localization of $\tilde{\phi}_\alpha$ near its charge Z_α leads to an exponential decrease of matrix elements that connect states of different separated atoms (ac) and (bc). This means that $V_{\alpha\beta}(\mathcal{R})$ in Eq. (8) are exponentially small for large $\mathcal{R}$ so that the equations for χ_α and χ_β are asymptotically split

$$\left[I\left(\frac{d^2}{d\mathcal{R}^2}+2ME\right)-V_{\alpha\alpha}\right]\chi_\alpha=0\ . \tag{8′}$$

Therefore, transformation $\mathbf{r}'\to\mathbf{r}=\mathbf{r}'\mathcal{R}$ explicitly singled out the operators $Q^{(0)}\mathcal{R}^{-1}\partial/\partial\mathcal{R}$ and $\mathcal{R}^{-2}K^{(0)}$, which are responsible for weak kinematical connection in channels a and b in the limit of separated atoms. This connection is influenced by the difference between $\mathcal{R}$ and Jacobi vectors $\mathbf{R}_a$ and $\mathbf{R}_b$ (cf. Fig. 1).

III. ASYMPTOTIC OF WAVE FUNCTION IN THE LIMIT OF SEPARATED ATOMS

A. Asymptotic form of two-center Hamiltonian

In this work we are interested in the behavior of wave function $\Psi=\Psi_a+\Psi_b$ for $\mathcal{R}\to\infty$ in the channels a and b. Since the connection between these channels is exponentially small, it is sufficient to examine asymptotics of one of the components, Ψ_b, for instance. In that case, it is suitable to state that vector $\mathbf{r}$ connects the light particle with nucleus b:

$$\mathbf{r}=\mathbf{r}_b\mathcal{R}=(\mathbf{r}'-\gamma_b\mathbf{e}_R)\mathcal{R}\ ,$$

$$\rho=1+\frac{m}{M}(\mathbf{r}'_b+\gamma_b\mathbf{e}_R)^2=\frac{m}{m_b}\rho_b\equiv\frac{\mu_b}{m_b}\rho_b\ .$$

Here

$$\rho_b=\left[1+2\frac{m_b}{M_b}r'_b\cos\theta_b+\frac{m_b}{M}r'^2_b\right]\ ,$$

$m=M_cM_b/(M_c+M_b)$ is reduced mass of muon in the (bc) atom, while $\mu_\beta=M_a(M_b+M_c)/(M_a+M_b+M_c)=(M^{-1}-m_bM_b^{-2})^{-1}$ is the reduced mass of nucleus a and atom (bc). We further transform variables $\mathbf{r}$ and $\mathcal{R}$ to new variables

$$\mathbf{r}_N=\sqrt{m_b/m}\,\mathbf{r},\quad \mathcal{R}_N=\sqrt{m_b/m}\,\mathcal{R}\equiv\sqrt{M/\mu_b}\mathcal{R}\ ,$$

which have a simple physical meaning for $\mathcal{R}\gg1$. Really, vector $\mathbf{r}_N$,

$$r_N=\sqrt{\rho_b}r_b=\left[1+\frac{m_b}{M_b}\frac{r_b}{R}\cos\theta_b\right]r_b\ , \tag{10}$$

for $r_b^{-1}R\gg1$ goes into Jacobi vector $\mathbf{r}_b$ of atom (bc) (Fig. 1), with the accuracy of $O((m_b/m)(r_b^2/R))$. Slow variable (Fig. 1), with the accuracy of $O((m_b/m)(r_b^2/R))$. Slow variable $\mathcal{R}_N$ for $r_b^{-1}R_b\gg1$,

$$\mathcal{R}_N=\sqrt{\rho_b}R=R_b^2+\frac{m_b}{\mu_b}r_b^2\approx\left[1+\frac{1}{2}\frac{m_b}{\mu_b}\frac{r_b^2}{R_b^2}\right]R_b\ , \tag{11}$$

becomes equal to the magnitude of the Jacobi vector $\mathbf{R}_b=\mathbf{R}+M_c(M_c+M_b)^{-1}\mathbf{r}_b=\mathbf{R}+(m_b/M_b)\mathbf{r}_b$ with an accuracy $O((m_b/\mu_b)r_b^2/R_b)$. After these substitutions, the following equation for $\tilde{\Psi}_b$ in the units $e=\hbar=m_b=1$ obtained (index N in $\mathcal{R}_N$ and $\mathbf{r}_N$ and index b in μ_b is omitted, in addition):

$$\left[-\frac{1}{2\mu}\frac{\partial^2}{\partial\mathcal{R}^2}+\frac{1}{\mu}Q^{(0)}\frac{1}{\mathcal{R}}\frac{\partial}{\partial\mathcal{R}}+\frac{4+K^{(0)}}{2\mu\mathcal{R}^2}+h_b-E\right]\tilde{\Psi}_b=0\ , \tag{12}$$

where Hamiltonian (9) takes the form

$$h_b=-\tfrac{1}{2}\rho_b^2\Delta_{\mathbf{r}}-\rho_b\left[\frac{2}{M_b}\frac{1}{\mathcal{R}}\frac{\partial}{\partial z}-\frac{2}{M}\frac{1}{\mathcal{R}^2}\right]Q^{(0)}+V+V_J-\frac{3}{2\mu\mathcal{R}^2}\ ,$$

$$V_J=\frac{\rho_b}{2M\mathcal{R}^2}(\mathbf{J}^2-l_+J_--l_-J_+-2J_z^2)-\frac{\rho_b}{2M_b\mathcal{R}^2}(p_+J_-+p_-J_+)\ ,$$

$$\rho_b=1+\frac{2}{M_b}\frac{z}{\mathcal{R}}+\frac{1}{M}\frac{r^2}{\mathcal{R}}\ ,$$

$$V=-\sqrt{\rho_b}\left[\frac{Z_b}{r}+\frac{Z_a}{|\mathbf{r}+\mathcal{R}\mathbf{e}_R|}-\frac{Z_rZ_b}{R}\right]\ .$$

Here $l_\pm=l_x\pm il_y$ and $p_\pm=\pm ip_x-p_y$ are spherical components of mesonic momentum and orbital angular momentum with respect to the nucleus b. A similar analysis was made previously in connection with an adiabatic study of the negative positronium ion[19] and electron-hydrogen and proton hydrogen scattering.[20]

B. Operator form of perturbation theory for the two-center problem

Let us now investigate the asymptotics of solutions $\phi_{ib}(\Omega;\mathcal{R})$ of the Hamiltonian

$$h_b\phi_{ib}(\Omega;\mathcal{R})=E_{ib}(\mathcal{R})\phi_{ib}(\Omega;\mathcal{R}) \tag{13}$$

near nucleus b. We look for the solutions of (13) in the form

$$\begin{aligned} E_{ib}(R)&=E_i^{(0)}+\mathcal{R}^{-1}E^{(1)}+\mathcal{R}^{-2}E^{(2)}+\cdots ,\\ \phi_{ib}(\Omega;\mathcal{R})&=\psi_i^{(0)}(\Omega)+\mathcal{R}^{-1}\psi^{(1)}+\cdots , \end{aligned} \tag{14}$$

where $E_i^{(0)}=-Z_b^2/2n^2$ and $\psi_i^{(0)}$ are the energy and the correct zeroth-order wave function of atom (bc) with principal quantum number n, respectively. The expansion of h_b for $r^{-1}\mathcal{R}\gg 1$, with the terms of order $\mathcal{R}^{-2}$ included, is

$$\begin{aligned} h_b=&h^{(0)}+Z_a(Z_b-1)\mathcal{R}^{-1}+V^{(1)}\mathcal{R}^{-1}+V^{(2)}\mathcal{R}^{-2}\\ &+(\mathbf{J}^2-2\boldsymbol{l}\cdot\mathbf{J})/(2M\mathcal{R}^2)+V_J^{(1)}\mathcal{R}^{-1}+V_J^{(2)}\mathcal{R}^{-2} , \end{aligned} \tag{15}$$

where

$$h^{(0)}=-\tfrac{1}{2}\Delta_r-Z_b/r,\quad V^{(1)}=-\frac{2}{M_b}\left[\frac{\partial}{\partial z}+z\left[\Delta_r+\frac{Z_b}{2r}\right]\right],$$

$$\begin{aligned} V^{(2)}=&gz-\left[\frac{1}{M}r^2-\frac{1}{M_b^2}z^2\right]\frac{Z_b}{2r}-\left[\frac{2}{M_b}\right]^2 z\frac{\partial}{\partial z}\\ &-\frac{1}{2}\left[\frac{2}{M}r^2+\left[\frac{2}{M_b}\right]^2 z^2\right]\Delta_r+\frac{2}{M}Q^{(0)}-\frac{3}{2\mu} , \end{aligned}$$

$$V_J^{(1)}=-\frac{1}{2M_b}(p_+J_-+p_-J_+) ,$$

$$V_J^{(2)}=-\frac{1}{M_b^2}z(p_+J_-+p_-J_+) .$$

The first term in $V^{(2)}$ corresponds to the linear Stark effect; $g=Z_a(M_b-1)M_b^{-1}+Z_aZ_bM_b^{-1}$ and $g=Z_a$ for $Z_b=1$.

In nth shell $\langle i\mid V^{(1)}\mid j\rangle=\langle i\mid V_J^{(1)}\mid j\rangle=0$, so that operators $V^{(1)}$ and $V_J^{(1)}$ can be represented in the form

$$V^{(1)}=[h^{(0)},v^{(1)}],\quad V_J^{(1)}=[h^{(0)},v_J^{(1)}] , \tag{16}$$

where

$$v^{(1)}=-\frac{1}{M_b}\left[r^2\frac{\partial}{\partial z}+2zQ^{(0)}\right] ,$$

$$v_J^{(1)}=-\frac{1}{M_b}\frac{i}{2}(r_+J_-+r_-J_+),\quad r_\pm=\pm ix-y .$$

The relations (16) permit removal of operator terms of order $\mathcal{R}^{-1}$ in the Hamiltonian (15) by means of isometrical transformation S:

$$\begin{aligned} h_b\to\tilde{h}_b=e^{iS}h_be^{-iS}\approx&h^{(0)}+Z_a(Z_b-1)\mathcal{R}^{-1}+i[S,h^{(0)}]\\ &+(V^{(1)}+V_J^{(1)})\mathcal{R}^{-1}+\tilde{\Lambda}\mathcal{R}^{-2} , \end{aligned}$$

$$\begin{aligned} \tilde{\Lambda}\mathcal{R}^{-2}=&(\mathbf{J}^2-2\boldsymbol{l}\mathbf{J})/(2MR^2)+(V^{(2)}+V_J^{(2)})\mathcal{R}^{-2}\\ &+i[S,(V^{(1)}+V_J^{(1)})]\mathcal{R}^{-1}+\frac{i^2}{2}[S,[S,h^{(0)}]] , \end{aligned} \tag{17}$$

$$\phi_{ib}\to\tilde{\phi}_{ib}=e^{iS}\phi_{ib}\approx[1+iS+\tfrac{1}{2}(iS)^2]\phi_{ib} ,$$

if the following condition is valid:

$$i[S,h^{(0)}]+(V^{(1)}+V_J^{(1)})\mathcal{R}^{-1}=0 ,$$

i.e., $iS=-(v^{(1)}+v_J^{(1)})\mathcal{R}^{-1}$.

As a result, the explicit expression for the equivalent operator $\tilde{\Lambda}$ is obtained:

$$\begin{aligned} &\tilde{\Lambda}=\Lambda^0+\Lambda^J,\quad \Lambda^{(0)}=V^{(2)}-V^{(1)}v^{(1)} ,\\ &\Lambda^J=(\mathbf{J}^2-2J_z^2)(2M)^{-1}-V_J^{(1)}v_J^{(1)}\\ &\qquad -(l_+J_-+l_-J_+)(2M)^{-1}+V_J^{(2)}\\ &\qquad -V^{(1)}v_J^{(1)}-V_J^{(1)}v^{(1)} . \end{aligned} \tag{18}$$

C. Dipole operator for the two-center problem

Eigenvalues and eigenfunctions of the equivalent operator $\tilde{\Lambda}$ describe the true corrections $E^{(2)}$ in expansion (14) and true zero-order wave functions $\tilde{\psi}^{(0)}$ of Hamiltonian $\tilde{h}_b$. The operator Λ^0 was calculated earlier in our work:[10]

$$\Lambda^0=-\frac{3}{2}\frac{n}{Z_b}gA_z+\frac{1}{2\mu}\frac{3}{2}l^2-\frac{1}{2\mu}(\tfrac{1}{2}n^2+4) , \tag{19}$$

where A_z and l^2 are the z projection of the Runge-Lenz vector and the squared value of the (bc)-atom orbital angular momentum, respectively. The calculation of the equivalent operator Λ^J is simplified because in the nth shell the relations of the type

$$\begin{aligned} V^{(1)}v=[h^{(0)},v]=&h^{(0)}v^2-vh^{(0)}v-v^2h^{(0)}\\ =&-vV^{(1)},\quad y\partial/\partial z=-z\partial/\partial y , \end{aligned}$$

etc., are valid. With these relations in mind, it is easy to obtain that

$$-V_J^{(1)}v^{(1)}-V^{(1)}v_J^{(1)}=-[V^{(1)},v^{(1)}]=\frac{2}{M_b^2}\left[z\frac{\partial}{\partial x}(J_--J_+)+iz\frac{\partial}{\partial y}(J_-+J_+)\right]$$

$$=-2V_J^{(1)}=\frac{1}{M_b^2}(l_+J_-+l_-J_+) ,$$

$$-V_J^{(1)}v_J^{(1)}=-\tfrac{1}{2}[V_J^{(1)}v^{(1)}]=-\frac{1}{2M_b^2}(\mathbf{J}^2-2J_z^2) .$$

By means of the relation $m_b/\mu_b = m_b/M - m_b^2/M_b^2$, we finally find

$$\Lambda^J = (2\mu)^{-1}(\mathbf{J}^2 - l_+J_- - l_-J_+ - 2J_z^2) , \tag{20}$$

i.e., in the second order of perturbation theory the true μ reduced mass is established near the centrifugal term.

Let us note that eigenfunctions of the Hamiltonian h_α, $\phi_{i\alpha}(\Omega;\mathcal{R}) \approx (1 - iS)\tilde{\psi}_i^{(0)}(\Omega) \approx \tilde{\psi}_i^{(0)}\Omega_\alpha$, coincide with eigenfunctions of separated atoms (αc) in the rotating coordinate system $x_\alpha y_\alpha z_\alpha$ with the z_α axis along the Jacobi vector $\mathbf{R}_\alpha$, i.e., $\Omega_\alpha = \{\mathbf{r}_\alpha, \Theta_\alpha, \phi_\alpha\}$. Really, operator $\mathcal{R}^{-1}v_J^{(1)} \approx -i\omega J_{\tilde{y}} = -(\omega/2)(\tilde{J}_+ - \tilde{J}_-)$ corresponds to a rotation of angle $\omega = \mathbf{R} \curvearrowright \mathbf{R}_\alpha$:

$$\sin\omega \approx M_c/(M_c + M_\alpha)\sqrt{x^2 + y^2} \approx \omega \ll 1$$

about the $\tilde{y}$ axis, which is perpendicular to the plane defined by three particles *abc* (cf. Fig. 2) (in the standard approach, such rotation can be performed only after the nonadiabatic connection is taken into account [formula (182) in the review article[5]]) and $\mathcal{R}^{-1}v^{(1)}$ transforms $\mathbf{r}_N$ into the Jacobi vector $\mathbf{r}_\alpha$ according to (11).

D. Eigensolutions of the dipole operator in parabolic coordinates

We shall look for the actual zeroth-order functions $\tilde{\psi}_i^{(0)}$ of the operator $\tilde{\Lambda}$ in the form of the linear combination

$$\tilde{\psi}_i^{(0)}(\Omega) = \sum_{m=(1-\sigma)/2}^{\min(J,n-1)} \sum_{n_2=0}^{n-m-1} a^i_{n_2 m} \psi^{Jm_J\lambda}_{n_1 n_2 m}(\Omega) ,$$

$$\psi^{Jm_J\lambda}_{n_1 n_2 m}(\Omega) = \varphi^{(0)}_{n_1 n_2 m}(\mu,\nu)\mathcal{D}^{J\lambda}_{mm_J}(\Phi,\Theta,\varphi) , \tag{21}$$

$$\mathcal{D}^{J\lambda}_{mm_J} = \left[\frac{2J+1}{16\pi(1+\delta_{m0})}\right]^{1/2} [(-1)^m D^J_{mm_J}(\Phi,\Theta,\varphi) + \sigma D^J_{-mm_J}(\Phi,\Theta,\varphi)]$$

of Coulomb parabolic functions[21] $\varphi^{(0)}_{n_1 n_2 m}(\mu,\nu)$, $\mu = r + z$, $\nu = r - z$ in the rotating coordinate system xyz (Fig. 2) in the representation of total momentum J.[5] Here, m_J is the projection of momentum J_Z on the Z axis of fixed coordinate system XYZ, $\lambda = \sigma(-1)^J$ is an eigenvalue of the inversion operator P_{tot}:($\mathbf{R} \to -\mathbf{R}$, $\mathbf{r} \to -\mathbf{r}$), $\sigma = \pm 1$ are eigenvalues of the reflection in the yz plane operator P_{yz}: ($\varphi \to \pi - \varphi$). It is easy to prove that the operator $\tilde{\Lambda}$ commutes with time constants of motion $\mathbf{J}^2$, J_Z, and P_{tot}. Then, eigenvalues $\tilde{\Lambda}_i$ and coefficients $a^i_{n_2 m}$ can be found from the secular equation

$$\sum_{m'=(1-\sigma)/2}^{\min(J,n-1)} \sum_{n_2'=0}^{n-m-1} [\langle n_1 n_2 m J m_J \lambda \mid \tilde{\Lambda} \mid n_1' n_2' m' J m_J \lambda\rangle - \tilde{\Lambda}_i \delta_{n_2 n_2'} \delta_{mm'}] a^i_{n_2' m'} = 0 , \tag{22}$$

where $i = \{Jm_J\sigma nq\}$, values q number in increasing order the solutions $\tilde{\Lambda}_i$ of the secular equation for fixed $Jm_J\lambda n$. In the case of $J \geq n-1$, the number of roots of Eq. (22) is equal to n^2. Part of them, $n(n+1)/2$ have parity $\lambda = +(-1)^J$, while for the rest of them parity is $\lambda = -(-1)^J$. The latter are degenerate with states of opposite parity in the limit of separated atoms. So we get that there exist $n(n+1)/2$ nondegenerate roots of (22) for fixed Jm_Jn [standard $(2J+1)$-fold degeneracy m_J remains]. The relations, which are necessary for the solution of the secular equation (22), can be easily composed from the known matrix elements.[22]

$$\langle n_1 n_2 m \mid A_z \mid n_1' n_2' m' \rangle = (n_2 - n_1)\delta_{n_2 n_2'}\delta_{mm'} ,$$

$$\langle n_1 n_2 m \mid l^2 \mid n_1' n_2' m' \rangle = \delta_{mm'}\{\tfrac{1}{2}[n^2 - 1 + m^2 - (n_1 - n_2)^2]\delta_{n_2 n_2'} - [(n_2+1)n_1(n_1+m)(n_2+m+1)]^{1/2}\delta_{n_2', n_2+1} - [n_2(n_1+1)(n_1+m+1)(n_2+m)]^{1/2}\delta_{n_2', n_2-1}\} ,$$

$$\langle n_1 n_2 m J m_J \lambda \mid l_+J_- \mid n_1\, n_2+1\, m-1\, J m_J \lambda\rangle = [(n_2+1)(n_1+m)]^{1/2}\gamma^{J\lambda}_{m,m-1} ,$$

$$\langle n_1 n_2 m J m_J \lambda \mid l_+J_- \mid n_1+1\, n_2\, m-1\, J m_J \lambda\rangle = -[(n_1+1)(n_2+m)]^{1/2}\gamma^{J\lambda}_{m,m-1} ,$$

$$\langle n_1 n_2 m J m_J \lambda \mid l_-J_+ \mid n_1\, n_2-1\, m+1\, J m_J \lambda\rangle = [n_2(n_1+m+1)]^{1/2}\gamma^{J\lambda}_{m,m+1} ,$$

$$\langle n_1 n_2 m J m_J \lambda \mid l_-J_+ \mid n_1-1\, n_2\, m+1\, J m_J \lambda\rangle = -[n_1(n_2+m+1)]^{1/2}\gamma^{J\lambda}_{m,m+1} ,$$

$$\langle n_1 n_2 m J m_J \lambda \mid \mathbf{J}^2 - 2J_z^2 \mid n_1' n_2' m' J m_J \lambda\rangle = [J(J+1) - 2m^2]\delta_{n_2 n_2'}\delta_{mm'} ,$$

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

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

$$\gamma^{J\lambda}_{00} = \gamma^{J\lambda}_{01} = \gamma^{J\lambda}_{10} = 0 \text{ for } \sigma = -1 .$$

The solution of the analogous secular equation in the channel a can be used to complete the entire classification of CAB in the limit of separated atoms.

E. Radial equations with weak kinematical coupling in the dipole approximation

In order to find asymptotics of wave function (12), it is better to use eigenfunctions of the operator $h_b+(2\mu\mathcal{R}^2)^{-1}K^{(0)}$ which is an explicit part of the Hamiltonian in Eq. (12). The equivalent operator $K^{(0)}$ in nth shell is equal to[10]

$$K^{(0)}=-\tfrac{1}{2}l^2+\tfrac{1}{2}n^2 ,$$

so that the respective equivalent operator $\Lambda=2\mu\tilde{\Lambda}+K^{(0)}$ has the form

$$\Lambda=-3\frac{n}{Z_b}\mu g A_z+\mathbf{L}^2 , \tag{23}$$

where

$$\mathbf{L}^2=(\mathbf{J}-\boldsymbol{l})^2=\mathbf{J}^2-l_+J_--l_-J_+-2J_z^2+l^2$$

is the squared value of the total orbital angular momentum of nucleus a relative to the atom (bc). Eigenfunctions $\psi_i^{(0)}$ of the operator Λ can be obtained from the secular equation (22) with the substitution of $\tilde{\Lambda}$ with Λ. Averaging (12) over these functions leads to an asymptotic system of equations, which allows us to find $\chi_{ib}(\mathcal{R})$ with the accuracy of $O(\mathcal{R}^{-1})$:

$$\left[\frac{d^2}{d\mathcal{R}^2}+2\mu E-V_{ii}(\mathcal{R})\right]\chi_{ib}(\mathcal{R})=\frac{2}{\mathcal{R}}\sum_j Q_{ij}^{(0)}\frac{d}{d\mathcal{R}}\chi_{jb}(\mathcal{R}) , \tag{24}$$

where

$$Q_{ij}^{(0)}=\tfrac{1}{2}\langle\psi_i^{(0)}\,|\,[h^{(0)},r^2]\,|\,\psi_j^{(0)}\rangle$$
$$=\tfrac{1}{2}(E_n^{(0)}-E_{n'}^{(0)})\langle\psi_i^{(0)}\,|\,r^2\,|\,\psi_j^{(0)}\rangle ,$$
$$V_{ii}(\mathcal{R})=2\mu[E_n^{(0)}+Z_a(Z_b-1)\mathcal{R}^{-1}]+\Lambda_i\mathcal{R}^{-2} .$$

The system of equations (24) can also be obtained from the Schrödinger equation for three particles in the Jacobi variables $\mathbf{R}_b,\mathbf{r}_b$ (cf. Fig. 1)

$$\left[-\frac{1}{2\mu}\frac{\partial^2}{\partial R_b}+h_b^{(0)}-\frac{Z_a}{|\mathbf{R}_b+(M_b-1)M_b^{-1}\mathbf{r}_b|}+\frac{Z_aZ_b}{|\mathbf{R}_b-M_b^{-1}\mathbf{r}_b|}+\frac{\mathbf{L}^2}{2\mu R_b^2}-E\right]\Psi_b=0 . \tag{25}$$

The vector $\mathbf{r}_b$ is given in the coordinate system with the z_b axis along the vector $\mathbf{R}_b$ (Fig. 2), $h_b^{(0)}=-\frac{1}{2}\Delta_{\mathbf{r}_b}-Z_b/r_b$, and volume element $d\tau_b=d\mathbf{r}_b dR_b\sin\Theta_b d\Theta_b d\Phi_b$. The asymptotic form (25) in the channel b agreed with an accuracy of $O(R_b^{-2})$ with the equation for the scattering problem of charged particle a on the atom (bc) in the dipole approximation[15]

$$\left[-\frac{1}{2\mu}\frac{\partial^2}{\partial R_b^2}+h_D-E\right]\Psi_b(\mathbf{R}_b,\mathbf{r}_b)=0 ,$$
$$h_D=h_b^{(0)}+Z_a(Z_b-1)R_b^{-1}+\Lambda_D/(2\mu R_b^2) , \tag{26}$$
$$\Lambda_D=-3(n/Z_b)\mu g A_{z_b}+\mathbf{L}^2 .$$

The transformation in this equation from R_b to $\mathcal{R}=(R_b^2+\mu^{-1}r_b^2)^{1/2}$ with an accuracy of $O(\mathcal{R}^{-2})$ and averaging over exact zeroth-order functions of h_D give the system of equations which coincides with (24).

It may seem, at first sight, that using the natural variables (1) only complicates the asympototic form (26) in the channel b, because the weak kinematical connection $\sim\mathcal{R}^{-1}\partial/\partial\mathcal{R}$ appears. But, this minimal complication is the consequence of unified description of channels a and b by means of the total orthogonal set CAB. This means that the suggested approach is without the characteristic strong channel coupling difficulty, and that the problem of the introduction of curvilinear coordinates in the adiabatic basis is solved. (The history of this problem can be found in the review article of Delos.[7])

F. Physical boundary conditions in the adiabatic representation

Let us show now how the physical boundary conditions for the scattering problem in the suitable coordinates can be created. To do that we examine the asymptotics of solutions of the system of equations (24) in the channel $i=|Jm_J\sigma nq\rangle$. Further, we shall restrict ourselves to the case $Z_a=Z_b=1$, which is the most important in mesoatomic physics. Leaving the main terms in (24), it is easy to obtain

$$\left[\frac{d^2}{d\mathcal{R}^2}+k_i^2\left[1-\frac{2\langle i\,|\,r^2\,|\,i\rangle}{2\mu\mathcal{R}^2}\right]-\frac{\Lambda_i}{\mathcal{R}^2}\right]\chi_{ib}(\mathcal{R})=0 ,$$
$$\frac{d}{d\mathcal{R}}\chi_{jb}(\mathcal{R})=\frac{k_i^2\langle i\,|\,r^2\,|\,j\rangle}{2\mu\mathcal{R}}\chi_{ib}(\mathcal{R}) . \tag{27}$$

The values i and j correspond to different n; $k_i^2=2\mu(E-E_i^{(0)})$, $E_i^{(0)}=-1/2n^2$. The following sum rule has been used:

$$2\sum_j\frac{Q_{ij}^{(0)}}{E_i^{(0)}}\frac{Q_{ji}^{(0)}}{E_j^{(0)}}=\langle i\,|\,r^2Q^{(0)}\,|\,i\rangle=\langle i\,|\,r^2\,|\,i\rangle .$$

The solution of Eq. (27) can be represented in the form $(k_i\langle i\,|\,r^2\,|\,j\rangle\ll 2\mu\mathcal{R})$

$$\chi_{ib}\approx B_i\sin\left[k_i\mathcal{R}\left[1-\frac{\langle i\,|\,r^2\,|\,i\rangle}{2\mu\mathcal{R}^2}-\frac{\Lambda_i}{2k_i^2\mathcal{R}^2}\right]+\delta_i\right]$$
$$\approx B_i\left[\sin\left[k_i\mathcal{R}-\frac{\Lambda_i}{2k_i\mathcal{R}}+\delta_i\right]-\frac{k_i\langle i\,|\,r^2\,|\,i\rangle}{2\mu\mathcal{R}}\cos\left[k_i\mathcal{R}-\frac{\Lambda}{2k_i\mathcal{R}}+\delta_i\right]\right] , \tag{28}$$
$$\chi_{jb}\approx -B_i\frac{k_i\langle i\,|\,r^2\,|\,j\rangle}{2\mu\mathcal{R}}\cos\left[k_i\mathcal{R}-\frac{\Lambda_i}{2k_i\mathcal{R}}+\delta_i\right],\quad j\neq i .$$

Here in the phase δ_i the phase shift δ_i^D, which appears because of the long-range dipole potential $\Lambda_i \mathcal{R}^{-2}$, can be separated explicitly: $\delta_i = \delta_i^D + \delta_i^C$, in accordance with quantum defect theory.[17] The explicit expression for δ_i^D is given in the Appendix. The scattering phase shift δ_i^C and amplitude B_i are obtained by means of a numerical solution of the adiabatic system of equations (8) with asymptotic conditions (28). Numerical algorithms were developed in the paper.[23] Using the completeness of the CAB, the following asymptotics of total wave function ψ in channel b is valid [with the accuracy of $O(\mathcal{R}^{-1})$]:

$$\Psi_b(\Omega,\mathcal{R}) \approx \left[\psi_i^{(0)}(\Omega_b)\chi_{ib}(\mathcal{R}) + \sum_{j(\neq i)} \psi_j^{(0)}(\Omega_b)\chi_{jb}(\mathcal{R})\right]\mathcal{R}^{-1}$$

$$= \psi_i^{(0)}(\Omega_b)\mathcal{R}^{-1}\left[\sin\left[k_i\mathcal{R} - \frac{\Lambda_i}{2k_i\mathcal{R}} + \delta_i\right] - \frac{k_i r_b^2}{2\mu\mathcal{R}}\cos\left[k_i\mathcal{R} - \frac{\Lambda_i}{2k_i\mathcal{R}} + \delta_i\right]\right]B_i \ .$$

If $k_i r_b^2 \ll 2\mu\mathcal{R}$,

$$\Psi_b(\Omega,\mathcal{R}) = \mathcal{R}^{-1}\psi_i^{(0)}(\Omega_b)\sin\left[k_i\left[\mathcal{R} - \frac{r_b^2}{2\mu\mathcal{R}}\right] - \frac{\Lambda i}{2k_i\mathcal{R}} + \delta_i\right]B_i \approx \mathcal{R}^{-1}\psi_i^{(0)}(\Omega_b)\sin\left[k_i R_b - \frac{\Lambda_i}{2k_i R_b} + \delta_i\right]B_i \ .$$

Therefore, we have shown, that the weak kinematical connection in Eqs. (24) leads to the establishment of the magnitude of the Jacobi vector $R_b \approx \mathcal{R} - r_b^2/(2\mu\mathcal{R})$ [cf. Eq. (11)] in the asymptotics of the total wave function (5) for large, but finite values of $\mathcal{R}$. This means that the asymptotics of the solutions of the adiabatic system of equations in suitable coordinates are in accordance with physical boundary conditions (29) of the scattering problem in channel b. It is evident that in channel a the physical boundary conditions are also satisfied because natural variables (1), in that case, transform into the respective Jacobi pair $\mathbf{R}_a, \mathbf{r}_a$ (cf. Fig. 1).

IV. SCATTERING AMPLITUDE IN THE DIPOLE APPROXIMATION

The possibility of a sufficiently simple establishing of physical boundary conditions with CAB is connected with the fact that the finiteness of the mass of particles a and b is taken into account from the beginning, contrary to the standard approach.[3,5] As a consequence of this, for the concrete scattering problem, it is necessary, to calculate the terms and wave functions of the two-center problem in suitable coordinates for every set of masses M_a and M_b. From this point of view, our approach is an apparent development of the hyperspherical adiabatic method, suggested in papers[8] for the description of helium-type systems with an infinite mass of nucleus. Phases δ_i and amplitudes B_i, obtained on the basis of a numerical solution of the adiabatic system of equations (8) with asymptotic condition (28), can be used for the calculation of low-energy cross sections for scattering processes in three-particle systems.

For inelastic atom ion scattering with changes of atomic orbital angular momentum, $|n\dot{l}\dot{m}_l\rangle \rightarrow |nlm_l\rangle$, phases and amplitudes are known, $\delta_i = \delta_i^D$, $B_i = 1$, if we are restricted to the dipole approximation.[15] This simple example permits us to demonstrate the connection between adiabatic asymptotics and the scattering amplitude for these transitions:

$$\Psi_{bkn\dot{l}\dot{m}_l}(\mathbf{R}_b,\mathbf{r}_b) \approx \sum_{l,m_l} \psi_{n_l m_l}^{(0)}(\mathbf{r}_b)[\delta_{ll}\delta_{m_l\dot{m}_l}e^{i\mathbf{k}R_b} + R_b^{-1}e^{ikr_b}f_{nlm_l,n\dot{l}\dot{m}_l}(\mathbf{N},\dot{\mathbf{N}})] \quad \text{as } r_b^{-1}R_b \rightarrow \infty .$$

Here unit vectors $\mathbf{N} = \mathbf{k}/k$ and $\dot{\mathbf{N}} = \mathbf{R}_b/R_b$ characterize directions of incoming and scattered waves, respectively. The quantization axis for orbital angular momenta is directed along vector $\dot{\mathbf{N}}$. Then, the scattering amplitude for the transition of atom bc from the state $|n\dot{l}\dot{m}_l\rangle$ to the state $|nlm_l\rangle$ can be represented in the form[15,24]

$$f_{nlm_l,n\dot{l}\dot{m}_l}(\mathbf{N},\dot{\mathbf{N}}) = \frac{4\pi}{2ik}\sum_{J,m_J,q}[e^{i[2\delta_q(J,k)-\pi J]}\phi_{n\dot{l}\dot{m}_l}^{*Jm_J\lambda q}(-\dot{\mathbf{N}}) - \phi_{n\dot{l}\dot{m}_l}^{*Jm_J\lambda q}(\dot{\mathbf{N}})]\phi_{nlm_l}^{Jm_J\lambda q}(\mathbf{N}) \ .$$

Values $\delta_q(J,k) = \delta_i^D + (\pi/2)J$ are eigenphases in the Λ representation, $i = \{Jm_J\sigma nq\}$; $\phi_{nlm_l}^{Jm_J\lambda q}(\mathbf{N})$ is the complete set of functions on unit sphere

$$\phi_{nlm_l}^{Jm_J\lambda q}(\mathbf{N}) = \sum_{L,m_L} U_{J\lambda}(q \mid lL)C_{Lm_L lm_l}^{Jm_J}Y_{Lm_L}(\mathbf{N})$$

which defines the eigenfunctions of the operator Λ in the fixed coordinate system:

$$\psi_i^{(0)}(\mathbf{r}_b,\mathbf{N}) = \sum_{l,m_l} \psi_{nlm_l}^{(0)}(\mathbf{r}_b)\phi_{nlm_l}^{Jm_J\lambda q}(\mathbf{N}) \ .$$

The coefficients $U_{J\lambda}(q \mid lL)$ are connected with the solutions $a_{n_2 m}^i$ of the secular equation for Λ (22), by means of the orthogonal transformation

$$U_{J\lambda}(q \mid lL) = \sum_{m=(1-\sigma)/2}^{\min(l,J)} \sum_{n_2=0}^{n-m-1} G_{mL}^{lJ\sigma} A_{nlm}^{n_1 n_2} a_{n_2 m}^{Jm_J\sigma nq} \ ,$$

where

$$G_{mL}^{lJ\sigma}=(-1)^{l+m}\frac{1+\sigma(-1)^{J-l-L}}{[2(1+\delta_{m0})]^{1/2}}C_{lmJ-m}^{L0}$$

is the Chang-Fano matrix.[24] This matrix connects the angular wave function in the fixed XYZ and rotating $x_by_bz_b$ coordinate systems (Fig. 2), while Tarter's matrix $A_{nlm}^{n_1n_2}$ connects Coulomb spherical and parabolical functions.[25] This transformation is characterized by total parity $\lambda=(-1)^{l+L}$ so that the necessary $a_{n_2m}^{Jm_J\sigma nq}$ are selected according to the condition $\sigma=(-1)^{J-l-L}$. The scattering amplitude for inelastic transitions with changes of principal quantum number n and for charge exchange processes can be created without difficulty on the basis of Refs. 24, 26, and 27.

V. CONCLUSIONS

In this paper we have developed the molecular adiabatic hyperspherical approach aimed at computing rotational states of three-particle mesic molecular systems with nonzero J, necessary for the description of processes involving muon catalysis of nuclear fusion, which has been investigated intensively in recent years. The asymptotics of such states for large $\mathcal{R}$ were thoroughly investigated for the first time. In that way, we extended the approach of Ref. 12.

For muonic molecular systems it is necessary to perform calculations in a molecular frame, and the asymptotics of solutions have to be much more accurately studied. In order to get the asymptotics in this case, we had to develop an original operator perturbation theory which is interesting in itself. The result of such a perturbation theory within the O(4,2) group[21] is a simple form of the secular equation for the dipole constant of motion in parabolic coordinates.

A substantially new result is the requantization of the orbital momentum of light particle to the true Jacobi vectors in each asymptotic channel. In that way we are able to formulate the correct scattering theory in the molecular frame.

Therefore we made use here of the molecular variant of hyperspherical coordinates, which is different from the variant suggested by Macek and Fano.[8] In our approach the molecular rotation is separated by means of simple symmetrized Wigner D functions. As a result, the determination of a hyperspherical adiabatic basis reduces to the solution of the system of $(J+1)$ two-dimensional equations. The suggested approach makes it possible to apply a highly effective finite element method for the calculation of the molecular hyperspherical bases. In this way highly excited eigenstates of the three-body problem could be successfully calculated.

Recently, at the Joint Institute for Nuclear Research (JINR), Dubna, a new numerical method of alternating subspaces has been developed.[13] Solutions of the two-center problem on a plane with this method are in progress and will be published elsewhere.

The compatible adiabatic basis was introduced in Ref. 9. This basis represents some generalization of hyperspherical adiabatic bases.[8] CAB can be constructed in different coordinate systems: spherical, thoroidal, and elliptic-cylindrical; generalized eliptic coordinates which were determined in Ref. 28. For example, toroidal coordinates for the three-body problem were introduced in a recent paper.[29]

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APPENDIX

The asymptotics of solutions of the Schrödinger equation with arbitrary dipole potential

$$\left[\frac{d^2}{d\mathcal{R}^2}-\frac{\Lambda_i}{\mathcal{R}^2}+k_i^2\right]\chi_i(\mathcal{R})=0$$

have the form[17]

$$\chi_i(\mathcal{R})\rightarrow \sin(k_i\mathcal{R}+\delta^D) \quad \text{as } \mathcal{R}\rightarrow\infty \ .$$

For

$$\Lambda_i\geq -\tfrac{1}{4}, \quad \lambda\equiv\lambda_R=-\tfrac{1}{2}+\sqrt{\tfrac{1}{4}+\Lambda_i} \ ,$$

$$\delta_i^D\equiv\frac{\pi}{2}\lambda_R \ .$$

In the case of $\Lambda_i<-\frac{1}{4}$, $\lambda\equiv\lambda_R+i\lambda_I=-\frac{1}{2}+i\sqrt{-\frac{1}{4}+|\Lambda_i|}$,

$$\delta^D=-\frac{\pi}{4}+\phi(k_i,\lambda_I) \ ,$$

$$\phi(k_i,\lambda_i)=\arctan\left\{\left[\tanh\left[\frac{\pi\lambda_I}{2}\right]\right]\tan\left[\lambda_I\ln\left[\frac{2}{k_i}\right]+\arg\Gamma(1+i\lambda_I)\right]\right\} .$$

(See Table I.)

TABLE I. Eigenvalues Λ_i of the operator Λ for the mesomolecule dt_μ ($l=\hbar=m_b=1$) in the channel b: $\mu=11.615\,17$, $g=1$, $n=4$ (calculations were performed by a program written by Abrashevich).

q/J	0	1	2	3	4	5	6
1	−415.18	−413.26	−409.43	−403.68	−396.01	−386.43	−374.93
2	−132.41	−272.81	−268.92	−263.09	−255.32	−245.61	−233.95
3	146.41	−130.44	−132.38	−126.47	−118.58	−108.78	−96.90
4	421.13	8.00	−126.50	−120.59	−112.72	−102.87	−91.06
5		148.43	12.00	6.01	14.02	24.03	36.04
6		284.81	146.39	17.99	25.98	35.96	47.95
7		423.27	152.49	152.48	160.59	170.73	182.90
8			288.92	158.56	166.67	176.80	188.95
9			427.44	295.09	303.32	313.61	325.95
10				433.71	442.06	452.51	465.04

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