Criteria for the validity of the diabatic-by-sector expansion in the hyperspherical coordinate method

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It is mathematically indicated that the widely used diabatic-by-sector recipe for solving coupled radial equations in the hyperspherical coordinate method causes non-negligible errors and these are revealed especially for extremely low-energy scattering. The intrinsic defects due to this method are illustrated for both bound state and the scattering states of $dt\mu$. The calculated results are also compared with those obtained by the adiabatic expansion method. [S1050-2947(97)08407-2]

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The hyperspherical coordinate method is recognized as an excellent method to study the Coulomb three-body problem in a unified manner. It covers conventional two-electron atoms, one-electron diatomic molecules, and even exotic atoms and molecules beyond the validity of the infinite nuclear mass approximation. It also enables one to compute precise scattering cross sections, resonance positions, and the widths as well as binding energies for several three-body systems [1]. In practical calculations with the hyperspherical approach, the diabatic-by-sector (DBS) method is widely applied [2]. In spite of the fact that the DBS method is successful in many actual problems we are unaware of rigid criteria for its validity. It is usually checked numerically by confirming the unitarity condition on the transformation matrices from one sector to the adjacent one when the sector size and number of channels are changed.

We have experienced in recent works [3,4] that the DBS method is by no means applicable to extremely low-energy collisions due to the slow convergence of calculated cross sections with respect to the number of channels included. Furthermore, this defect is never remedied by simply employing a smaller sector size. In the present article we ascertain a source of such difficulties by deriving an alternative set of coupled radial equations from those originally given by the DBS method. The resulting equations correspond to those obtained by the adiabatic (AD) expansion method. The validity of the DBS method is then discussed with reference to calculations using both the DBS and AD methods for the binding energies and the scattering cross sections of the $dt\mu$ system.

We begin with the coupled radial equations of the DBS method, given by

$$\widetilde{\mathbf{F}}(\rho)'' + \left[\frac{1}{4\rho^2} + 2[E - \widetilde{\mathbf{U}}(\rho)]\right]\widetilde{\mathbf{F}}(\rho) = \mathbf{0}, \tag{1}$$

where an $N\times N$ matrix notation has been adopted for the radial wave function $\widetilde{\mathbf{F}}$ and diabatic coupling matrix $\widetilde{\mathbf{U}}$. The quantities E and ρ are the total energy and hyperradius, respectively. Hereafter the dimension N is assumed finite and the infinite dimension is expressed as N_∞. Equation (1) is defined within a small sector of ρ, $\rho_m - \Delta\rho/2 < \rho < \rho_m + \Delta\rho/2$, where ρ_m gives the midpoint of the sector and $\Delta\rho$ its width.

A set of channel wave functions having a truncated dimension of $1\times N$ is defined as $\{\mathbf{\Phi}\}$, each component of which is a solution of the associated adiabatic equation

$$\hat{U}(\rho,\Omega)\mathbf{\Phi}(\rho,\Omega) = \mathbf{\Phi}(\rho,\Omega)\mathbf{U}(\rho), \tag{2}$$

with $\hat{U}$ and $\mathbf{U}$ the adiabatic Hamiltonian and the $N\times N$ diagonal adiabatic potential matrix, respectively. The symbol Ω denotes all relevant hyperangles. A complete set of the adiabatic channel wave functions with the dimension of $1\times N_\infty$ is denoted by $\{\mathbf{\Phi}_\infty\}$. The matrix $\{\mathbf{\Phi}\}$ spans a subspace of $\{\mathbf{\Phi}_\infty\}$. Also let the associated adiabatic potential matrix be $\mathbf{U}_\infty$.

The total wave function $\mathbf{\Psi}$ represented by the $1\times N$ dimension matrix is written

$$\mathbf{\Psi}(\rho,\Omega) = \mathbf{\Phi}(\rho_m,\Omega)\widetilde{\mathbf{F}}(\rho), \tag{3}$$

following the DBS ansatz. Equation (1) results from Eq. (3) and thus $\widetilde{\mathbf{U}}$ is of the form

$$\begin{aligned}\widetilde{\mathbf{U}}(\rho) &= \langle \mathbf{\Phi}(\rho_m,\Omega)|\hat{U}(\rho,\Omega)|\mathbf{\Phi}(\rho_m,\Omega)\rangle \\ &= \mathbf{C}^\dagger(\rho)\mathbf{U}_\infty(\rho)\mathbf{C}(\rho),\end{aligned} \tag{4}$$

where it is understood that integrations are done over Ω. In the second equality we have used the completeness property of $\{\mathbf{\Phi}_\infty\}$ and defined the $N_\infty\times N$ matrix $\mathbf{C}$ as $\mathbf{C}(\rho) = \langle \mathbf{\Phi}_\infty(\rho,\Omega)|\mathbf{\Phi}(\rho_m,\Omega)\rangle$.

It is convenient to partition $\mathbf{C}$ into two block matrices consisting of a $N\times N$ matrix $\mathbf{A}$ and a residual $(N_\infty - N)\times N$ matrix $\mathbf{A}_R$ as

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$$\mathbf{C}(\rho)=\begin{pmatrix}\mathbf{A}(\rho)\\ \mathbf{A}_R(\rho)\end{pmatrix}, \tag{5}$$

where $\mathbf{A}$ is given by

$$\mathbf{A}(\rho)=\langle\mathbf{\Phi}(\rho,\Omega)|\mathbf{\Phi}(\rho_m,\Omega)\rangle. \tag{6}$$

Substituting Eq. (5) into Eq. (4), $\tilde{\mathbf{U}}$ gives

$$\tilde{\mathbf{U}}(\rho)=\mathbf{A}^{\dagger}(\rho)\mathbf{U}(\rho)\mathbf{A}(\rho)+\mathbf{A}_R^{\dagger}(\rho)\mathbf{U}_R(\rho)\mathbf{A}_R(\rho), \tag{7}$$

where the $N_\infty\times N_\infty$ matrix $\mathbf{U}_\infty$ has been partitioned into two diagonal matrices $\mathbf{U}$ of dimension $N\times N$ and the remaining one $\mathbf{U}_R$ with dimension $(N_\infty-N)\times(N_\infty-N)$.

An alternative radial wave function with the dimension of $N\times N$ is defined as

$$\mathbf{F}(\rho)=\mathbf{A}(\rho)\tilde{\mathbf{F}}(\rho). \tag{8}$$

Inserting Eq. (7) and the inverse expression $\tilde{\mathbf{F}}=\mathbf{A}^{-1}\mathbf{F}$ into Eq. (1) yields coupled radial equations for $\mathbf{F}$,

$$\mathbf{F}''+2\mathbf{A}(\mathbf{A}^{-1})'\mathbf{F}'+\left[\frac{1}{4\rho^2}+\mathbf{A}(\mathbf{A}^{-1})''+2(E-\mathbf{A}\mathbf{A}^{\dagger}\mathbf{U}-\mathbf{A}\mathbf{A}_R^{\dagger}\mathbf{U}_R\mathbf{A}_R\mathbf{A}^{-1})\right]\mathbf{F}=\mathbf{0}, \tag{9}$$

where the argument ρ has been omitted.

It is assumed that the sector size $\Delta\rho$ is sufficiently small that $\mathbf{\Phi}(\rho,\Omega)$ may be expanded in a Taylor series with respect to $\delta\rho=\rho-\rho_m$ ($|\delta\rho|\leqslant\Delta\rho$),

$$\mathbf{\Phi}(\rho,\Omega)=\mathbf{\Phi}(\rho_m,\Omega)+\mathbf{\Phi}(\rho_m,\Omega)'\,\delta\rho+\frac{1}{2}\mathbf{\Phi}(\rho_m,\Omega)''\delta\rho^2+\cdots. \tag{10}$$

Then the matrix $\mathbf{A}$ becomes

$$\mathbf{A}(\rho)=\mathbf{1}+\mathbf{P}^{\dagger}(\rho_m)\,\delta\rho+\frac{1}{2}\mathbf{W}^{\dagger}(\rho_m)\,\delta\rho^2+\cdots, \tag{11}$$

where derivative matrices $\mathbf{P}$ and $\mathbf{W}$ have been defined as $\mathbf{P}(\rho)=\langle\mathbf{\Phi}(\rho,\Omega)|d\mathbf{\Phi}(\rho,\Omega)/d\rho\rangle$ and $\mathbf{W}(\rho)=\langle\mathbf{\Phi}(\rho,\Omega)|d^2\mathbf{\Phi}(\rho,\Omega)/d\rho^2\rangle$, respectively. Note that $\mathbf{A}$ is not unitary since $N\neq N_\infty$. The matrices $\mathbf{A}^{-1}$ and $\mathbf{A}^{\dagger}$ are of the following forms:

$$\mathbf{A}^{\dagger}(\rho)=\mathbf{1}+\mathbf{P}(\rho_m)\,\delta\rho+\frac{1}{2}\mathbf{W}(\rho_m)\,\delta\rho^2+\cdots \tag{12}$$

and

$$\mathbf{A}^{-1}(\rho)=\mathbf{1}+\mathbf{P}(\rho_m)\,\delta\rho-\frac{1}{2}\{\mathbf{W}^{\dagger}(\rho_m)-2\mathbf{P}(\rho_m)^2\}\,\delta\rho^2+\cdots$$
$$=\mathbf{1}+\mathbf{P}(\rho_m)\,\delta\rho+\frac{1}{2}\{\mathbf{W}(\rho_m)-2\mathbf{\Delta}(\rho_m)\}\,\delta\rho^2+\cdots, \tag{13}$$

respectively. In the second equality of Eq. (13), we have used the identity $\mathbf{W}^{\dagger}(\rho)+\mathbf{W}(\rho)=2\mathbf{W}_S(\rho)$ and the definition $\mathbf{\Delta}(\rho)=\mathbf{W}_S(\rho)+\mathbf{P}^{\dagger}(\rho)\mathbf{P}(\rho)$ with the symmetric matrix $\mathbf{W}_S$ defined as $\mathbf{W}_S(\rho)=-\langle d\mathbf{\Phi}(\rho,\Omega)/d\rho|d\mathbf{\Phi}(\rho,\Omega)/d\rho\rangle$. If the complete set $\{\mathbf{\Phi}_\infty\}$ is inserted into $\mathbf{W}_S(\rho)$, this matrix is given by $\mathbf{W}_S(\rho)=-\langle\mathbf{\Phi}_\infty(\rho,\Omega)|d\mathbf{\Phi}(\rho,\Omega)/d\rho\rangle^{\dagger}\langle\mathbf{\Phi}_\infty(\rho,\Omega)|d\mathbf{\Phi}(\rho,\Omega)/d\rho\rangle$. Therefore, in the limit that N tends to infinity, $\mathbf{\Delta}(\rho)$ vanishes and Eq. (13) coincides with Eq. (12).

Employing Eqs. (11)–(13) in Eq. (9) and neglecting contributions from higher-order terms of $\delta\rho$ gives

$$\mathbf{F}(\rho)''+2\mathbf{P}(\rho_m)\mathbf{F}(\rho)'+\left[\frac{1}{4\rho^2}+[\mathbf{W}(\rho_m)-2\mathbf{\Delta}(\rho_m)]+2[E-\mathbf{U}(\rho)]\right]\mathbf{F}(\rho)=\mathbf{0}, \tag{14}$$

where the fact that $\mathbf{A}_R$ in Eq. (9) is of the order of $\delta\rho$ has been taken into account. On the other hand, expanding $\mathbf{\Psi}$ as

$$\mathbf{\Psi}(\rho,\Omega)=\mathbf{\Phi}(\rho,\Omega)\mathbf{F}_{\mathrm{AD}}(\rho), \tag{15}$$

following the AD expansion method instead of Eq. (3), one finds for the coupled radial equations of the wave function $\mathbf{F}_{\mathrm{AD}}$ with the $N\times N$ dimension the result

$$\mathbf{F}_{\mathrm{AD}}(\rho)''+2\mathbf{P}(\rho)\mathbf{F}_{\mathrm{AD}}(\rho)'+\left[\frac{1}{4\rho^2}+\mathbf{W}(\rho)+2[E-\mathbf{U}(\rho)]\right]\mathbf{F}_{\mathrm{AD}}(\rho)=\mathbf{0}. \tag{16}$$

Here no approximations have been employed so far aside from truncating the dimension of the equations to N.

The quasiadiabatic equation (14) differs from Eq. (16) in that (i) the nonadiabatic coupling terms of $\mathbf{P}(\rho_m)$ and $\mathbf{W}(\rho_m)$ are constant within the sector and (ii) the correct coupling $\mathbf{W}(\rho)$ is replaced by $\mathbf{W}(\rho_m)-2\mathbf{\Delta}(\rho_m)$. This defect (i) is remedied in principle by making the sector size $\Delta\rho$ smaller. In practice, however, this problem becomes more acute in the case where the couplings $\mathbf{P}(\rho)$ and $\mathbf{W}(\rho)$ vary sharply and rapidly within the sector and these values are never regarded as constant. Such rapid variations usually occur in the distant region of ρ where energy levels of different channels cross, giving rise to Landau-Zener-type couplings. The defect (ii) indicates that the DBS method does not satisfy the correct asymptotic conditions for scattering wave functions, a drawback that is most significant in the lower-incident-energy region.

The asymptotic conditions in the hyperspherical coordinate method are determined by the behavior of diagonal elements of $\mathbf{W}$, $\mathbf{U}$ and the mock potential $1/4\rho^2$ at large ρ [5]. An error in the DBS method is of the order $\sim a/\rho^2$ with a negative constant a given by the asymptotic form of $\mathbf{\Delta}$, independently of the sector size. This defect is remedied only by increasing the number of channels and letting $\mathbf{\Delta}$ become

TABLE I. Binding energies (eV) for a ground state ($J=0,\ v=0$) and the first excited state ($J=0,\ v=1$) of the $dt\mu$ molecule in the $n=1$ manifold. These are reckoned from the threshold energy of the $t\mu(1s)$ fragment. J and v mean the total angular momentum and the vibrational quantum numbers, respectively. DBS and AD represent the present diabatic-by-sector and adiabatic calculations, respectively. N is the number of channels included.

States	N	DBS	AD	Other works
(0,0)	1	333.22	317.75	317.75 [7]
	2	333.18	317.80	317.80 [7]
	6	322.20	319.00	
	12	320.77	319.09	
	20	320.18	319.11	
	Exact			319.139752161 [8]
(0,1)	1	43.851	31.982	31.99 [7]
	2	42.789	33.446	33.46 [7]
	6	36.835	34.634	
	12	36.059	34.755	
	20	35.723	34.788	
	Exact			34.8344647 [8]

negligibly small. As illustrated in the following, however, the convergence with respect to the number of channels is quite slow in practice.

The defect (ii) of the DBS appoach is exemplified by comparing actual calculated results by both the DBS and AD methods. To this end, we focus on the binding energies and the scattering cross sections of the $dt\mu$ system with the total angular momentum $J=0$ in the $n=1$ manifold. Results together with the corresponding reported data are shown in Tables I and II. The AD method is that discussed in Refs. [3,4]. Computational conditions are set equal for both methods. The physical values employed here for masses and the Rydberg constant have been taken from [6].

As seen in Table I the binding energies obtained by the DBS method converge so slowly that errors incurred remain large even in the maximum channel ($N=20$) calculations, where the DBS results are still worse than the AD ones by one unit. In addition, the tendencies of convergence are opposite in both methods. That is, convergence is from below in the DBS method and from above in the AD method. While the former does not satisfy the variational principle, the latter does strictly.

The reason for the opposite direction of convergence in the DBS method is easily understood from the properties of the error $\mathbf{\Delta}$ in Eq. (14). Its diagonal elements are negative definite and act on an effective adiabatic potential so that the depth becomes shallower with increasing N.

The difficulties in the DBS method are further exacerbated in the scattering calculations at extremely low energies. The diagonal element of $\mathbf{\Delta}$ behaves asymptotically as a spurious attractive dipole potential $\sim -|a|/\rho^2$ as mentioned above and spoils the scattering asymptotic conditions to some extent. Such a breakdown makes it difficult to extract accurate cross sections, though it would affect the binding energy calculations only slightly. Especially, it is noticeable for low-energy scattering in the $n=1$ manifold, where an effective asymptotic potential of the fragment channel is dominated by a polarization potential $\sim 1/\rho^4$ much weaker than the spurious dipole one. Even if the leading contribution of the asymptotic potential is from the Coulomb potential $\sim 1/\rho$, the spurious dipole potential could still cause noticeable errors.

TABLE II. Cross sections (cm^2) for the elastic scattering $t+d\mu(1s)$ with $J=0$ versus the center-of-mass incident energies E (eV) reckoned from the threshold energy of the $d\mu(1s)$ fragment. Values in square brackets mean the powers of 10.

E	DBS	AD	Other work [9]
1	1.846[−18]	9.229[−20]	9.322[−20]
3	4.379[−19]	1.284[−19]	1.277[−19]
5	2.617[−19]	1.351[−19]	1.357[−19]
8	1.732[−19]	1.346[−19]	1.346[−19]
10	1.529[−19]	1.303[−19]	1.302[−19]
30	6.496[−20]	6.873[−20]	6.995[−20]
50	3.047[−20]	3.082[−20]	3.216[−20]

Table II shows the elastic cross sections of $t+d\mu(1s)$ in the range of the center-of-mass incident energies from 1 to 50 eV. Note that this energy range should be considered as relatively low since 1 eV equals 1.78×10^{-4} in the muon atomic unit. Both calculations by the DBS and the AD methods incorporate 20 channels. The cross sections obtained by the former method are overestimated in the lower-energy region due to the presence of the spurious long-range potential $\mathbf{\Delta}$. These reach the magnitude of cross sections comparable with those by the AD method at energies no less than the order of 10 eV. The cross sections by the DBS method were found to be considerably overestimated specifically in the extremely low-energy region from 0.001 to 0.1 eV, where the $dt\mu$ molecule plays decisive roles in the muon-catalyzed fusion. As to the elastic process of $d+t\mu(1s)$ and the muon transfer process from $d\mu(1s)$ to $t\mu(1s)$, similar tendencies to Table II were observed.

To summarize, we derived a set of quasiadiabatic coupled radial equations from those given in the DBS method and compared it with the exact form of the corresponding AD equations. We found it likely that the DBS method causes non-negligible errors due to its intrinstic defects that the couplings $\mathbf{P}(\rho)$ and $\mathbf{W}(\rho)$ are approximated as constant even when varying sharply and rapidly within the sector and that this method does not guarantee to satisfy the correct scattering asymptotic conditions. The general discussion was illustrated using computed binding energies and the scattering cross sections of the $dt\mu$ system in the $n=1$ manifold. Finally it is mentioned that recently an attempt has been made to remedy the drawbacks in the DBS method analyzed in the present article [10].

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