PHYSICAL REVIEW A VOLUME 41, NUMBER 3 1 FEBRUARY 1990

Two-body fragmentation channels of three-body systems

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(Received 10 August 1989)

An asymptotic expansion of the wave functions for the fragmentation channels of three-body systems is developed in hyperspherical coordinates. It is shown that, to any finite power in $1/R$, where $mR^2=\sum_i m_i r_i^2$ is the trace of the inertia tensor, the expanded wave function is an analytic finite sum of Sturmian functions. The expansion is carried out explicitly through order $1/R^4$. These asymptotic states converge (as $R\rightarrow\infty$) to polarized orbitals for two-electron systems, and also provide improved dissociation channels for molecular ions, such as HD^+. Asymptotic potential curves for He and μ^--H systems are presented as illustrations.

I. INTRODUCTION

The hyperspherical adiabatic approximation[1] has been quite successful in reproducing spectral characteristics of He and its isoelectronic ions [2] of Ps^-,[3] and of the molecular ions H_2^+ and HD^+.[4,5] The utility of the variable $R=(\sum_i m_i r_i^2/m)^{1/2}$ as a generic reaction coordinate for three-body systems with disparate mass and charge characteristics appears quite fortuitous, and despite the existence of a formally complete coupled-channel expansion, has not been further justified. Rather, the observed similarity between atomic and molecular spectra and the hyperspherical theory suggests that adiabaticity does not hinge on the small mass (or velocity) ratios of molecular constituents, but applies generally to any complex formed by particles with long-range Coulomb interactions.[6] In essence, a much higher degree of elasticity is observed in collisions of electrons, atoms, and molecules than can be justified on the basis of small mass ratios alone.

Macek's original calculation of the doubly excited states of helium illustrates the main conceptual advantages of the hyperspherical adiabatic method.[1] The use of a reaction coordinate which is symmetric with respect to interchange of the electron pair ensures correct representation of the wave function in the reaction zone.[7] This symmetry of R under electron interchange is a special case of the more general invariance of R with respect to the "kinematic rotations" attendant to any rearrangement process, regardless of the particle masses.[8] In addition, R tends to an independent particle coordinate in the limit of fragmentation, providing a connection with the standard close-coupling expansion at large distances.[9] In summary, the hyperspherical adiabatic representation incorporates the exchanges of momentum and angular momentum characteristic of the reaction zone, while converging to the polarized orbitals of the fragmentation zone.[10]

In accord with this emphasis on the correct representation of reaction and fragmentation channels, a number of attempts have been made to obtain analytic solutions of the hyperspherical equations in the limiting regions $R\rightarrow 0$ and $R\rightarrow\infty$, respectively. In the case of three-body systems with two light-mass particles or three equal-mass particles, a harmonic expansion[2] about $R=0$ has been pushed to much larger radii,[3] now even approaching the fragmentation zone. For systems with two heavy particles, a single-center expansion has been used to calculate accurate small-R potential curves[4] and to demonstrate their near equivalence to Born-Oppenheimer curves.

An asymptotic expansion in the fragmentation zone has, on the other hand, been restricted to zeroth-order perturbation theory.[1] The exception to this statement is Ref. 9, in which an expansion in powers of $1/R^2$ was used to demonstrate the convergence of the hyperspherical adiabatic representation of two-electron systems to the polarized orbitals of the close-coupling method.

Our primary purpose here is to generalize the results of Ref. 9 to three-body systems with arbitrary masses. This should be of some use to theorists studying muonic (and other) three-body systems employing the adiabatic hyperspherical approach. In Sec. IV C below we present some sample results of our asymptotic forms for the $(p^+\mu^-)e^-$ system.

A secondary motivation for this study is the eventual link of the $1/R$ expansion with the hyperspherical harmonic expansion about $R=0$. The successful joining of these two expansions for two-electron systems would eliminate the need for tabulating numerical channel functions and would expedite the calculation of physical observables within the adiabatic approximation. The degree to which this link has been achieved is also discussed in Sec. IV C.

As a longer-range goal, it is possible to improve upon the adiabatic solutions by solving the coupled radial equations analytically in the fragmentation zone. This was accomplished to order $1/R^2$ in Ref. 11. Extension of that work using the results of this paper would cast the entire fragmentation zone wave function into essentially analytic form, substantially reducing the radius over which numerical calculations need be performed. This development hinges upon, but remains beyond the scope of, this article.

Finally, we note that the present article contains some small corrections to the results of Ref. 9. It is found below that a fully consistent expansion must be performed in powers of $1/R$, as opposed to the $1/R^2$ expansion used previously. This does not alter the results of Ref. 9 for the ground-state channel, though it does affect excited-state channels. In addition, two small terms of order $1/R^4$, omitted earlier, are included herein. In order to include the above corrections, an alternative notation to that of Ref. 9 is used throughout this work.

II. ASYMPTOTIC FORM OF SCHRÖDINGER'S EQUATION

The hyperspherical coordinate form of Schrödinger's nonrelativistic equation, and the large-R form of the Hamiltonian operator, are presented below. Atomic units (a.u.) will be used throughout. Where applicable, the mass of the electron ($m_e=1$ a.u.) will be specified explicitly to maintain symmetry in the equations.

A. Schrödinger's equation in hyperspherical coordinates

We consider a system of three particles ($i=1,2,3$) with arbitrary masses m_i and charges Z_i interacting via Coulomb forces. Only systems possessing two-body bound states, i.e., with

$$Z_1Z_2<0 , \tag{1}$$

will be considered. The nonrelativistic Hamiltonian for this system is

$$H=\sum_{i=1}^{3}\left[-\frac{1}{2m_i}\nabla^2_{\mathbf{r}_i}\right]+\sum_{\substack{i,j\\ i<j}}\frac{Z_iZ_j}{|\mathbf{r}_i-\mathbf{r}_j|} . \tag{2}$$

The center-of-mass kinetic energy is extracted from Eq. (2) by transforming to relative coordinates, the choice of which is usually based upon the fragmentation process of interest. For fragmentation channels associated with the two-body bound states resulting from Eq. (1), we choose the Jacobi coordinates

$$\begin{aligned}\mathbf{r}_{12}&=\mathbf{r}_2-\mathbf{r}_1 ,\\ \mathbf{r}_{12,3}&=\mathbf{r}_3-\frac{m_1\mathbf{r}_1+m_2\mathbf{r}_2}{m_1+m_2} ,\\ \mathbf{r}_{\rm cm}&=\frac{1}{M}(m_1\mathbf{r}_1+m_2\mathbf{r}_2+m_3\mathbf{r}_3) ,\end{aligned} \tag{3}$$

with associated reduced masses

$$\begin{aligned}m_{12}&=\frac{m_1m_2}{m_1+m_2} ,\\ m_{12,3}&=\frac{(m_1+m_2)m_3}{M}\\ M&=m_1+m_2+m_3 .\end{aligned} \tag{4}$$

Upon separation of the center-of-mass motion, Schrödinger's time-independent wave equation is

$$H\Psi=E\Psi , \tag{5}$$

where

$$H=-\frac{1}{2m_{12}}\nabla^2_{\mathbf{r}_{12}}-\frac{1}{2m_{12,3}}\nabla^2_{\mathbf{r}_{12,3}}+\frac{Z_1Z_2}{r_{12}}+\frac{Z_1Z_3}{|\mathbf{r}_{12,3}+m_{12}\mathbf{r}_{12}/m_1|}+\frac{Z_2Z_3}{|\mathbf{r}_{12,3}-m_{12}\mathbf{r}_{12}/m_2|} , \tag{6}$$

and where E is the total energy in the center-of-mass frame.

The hyperspherical radius R is defined in terms of the trace of the inertia tensor,[8] specifically,

$$mR^2=\tfrac{1}{2}\mathrm{Tr}(\underline{I}) , \tag{7}$$

where $\underline{I}$ represents the inertia tensor. In the center-of-mass frame, with the relative coordinates defined in Eq. (3), the explicit form of Eq. (7) is

$$mR^2=m_{12}r_{12}^2+m_{12,3}r_{12,3}^2 . \tag{8}$$

The parameter m is included for dimensional clarity, but its magnitude is arbitrary since it simply sets the scale of R. As mentioned in the Introduction, the trace of the inertia tensor is independent of the choice of Jacobi vectors, which we made in Eq. (3). A second coordinate α, which depends on this choice, is defined as a ratio of the lengths of the Jacobi vectors, specifically,

$$\tan\alpha=\left[\frac{m_{12}}{m_{12,3}}\right]^{1/2}\frac{r_{12}}{r_{12,3}} . \tag{9}$$

The coordinate transformation $(\mathbf{r}_{12},\mathbf{r}_{12,3})\rightarrow(R,\alpha,\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})$, applied to Schrödinger's equation, Eq. (5), yields

$$\left[-\frac{1}{2m}\left[\frac{\partial^2}{\partial R^2}-\frac{15}{4R^2}-\frac{\Lambda^2}{R^2}\right]-\frac{C(\alpha,\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})}{2mR}\right]\psi=E\psi , \tag{10}$$

where a reduced wave function

$$\psi=R^{5/2}\Psi \tag{11}$$

has been introduced to eliminate a first derivative term. The operator Λ^2 in Eq. (10) is the Casimir invariant of the six-dimensional rotation group. It has the explicit differential form

$$\Lambda^2=-\frac{1}{(\sin^2\alpha)(\cos^2\alpha)}\frac{\partial}{\partial\alpha}(\sin^2\alpha)(\cos^2\alpha)\frac{\partial}{\partial\alpha}+\frac{\mathbf{L}_{12}^2}{\sin^2\alpha}+\frac{\mathbf{L}_{12,3}^2}{\cos^2\alpha}\ , \tag{12}$$

where $\mathbf{L}_{12}$ and $\mathbf{L}_{12,3}$ are the angular momentum operators associated with $\hat{\mathbf{r}}_{12}$ and $\hat{\mathbf{r}}_{12,3}$, respectively.

The factor $-C/2mR$ in Eq. (10) is equal to the three potential-energy terms on the right-hand side of Eq. (6). The explicit form of $C(\alpha,\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})$ is

$$C(\alpha,\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})=-\frac{2Z_1Z_2\sqrt{m}\sqrt{m_{12}}}{\sin\alpha}-\frac{2Z_1Z_3\sqrt{m}\sqrt{m_{12,3}}}{|(\cos\alpha)\hat{\mathbf{r}}_{12,3}+\sqrt{(m_2m_3/m_1M)}(\sin\alpha)\hat{\mathbf{r}}_{12}|}-\frac{2Z_2Z_3\sqrt{m}\sqrt{m_{12,3}}}{|(\cos\alpha)\hat{\mathbf{r}}_{12,3}-\sqrt{(m_1m_3/m_2M)}(\sin\alpha)\hat{\mathbf{r}}_{12}|}\ . \tag{13}$$

The operators Λ^2 and C in Eqs. (12) and (13) do not commute, reflecting the nonseparability of Eq. (10).

Macek[1] defined a set of basis functions as solutions of the equation obtained by disregarding the $\partial^2/\partial R^2$ term in Eq. (10),

$$[\Lambda^2+4-RC(\Omega)]\Phi_\mu(R;\Omega)=2mR^2U_\mu(R)\Phi_\mu(R;\Omega)\ , \tag{14}$$

where $\Omega=\{\alpha,\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3}\}$. A factor of $2m$ has been included above (unlike standard references) so that $U_\mu(R)$ is expressed in atomic units. The solutions of Eq. (10) can then be expanded in the form

$$\psi_E(R,\Omega)=\sum_\mu F_E^\mu(R)\Phi_\mu(R;\Omega)\ , \tag{15}$$

resulting in the coupled system of equations

$$\left[\frac{d^2}{dR^2}+2m[E-U_\mu(R)]+\frac{1}{4R^2}\right]F_E^\mu(R)=-\sum_{\mu'}W_{\mu'}^\mu(R)F_E^{\mu'}(R)\ , \tag{16}$$

where

$$W_{\mu'}^\mu(R)=\left[\Phi_\mu,\frac{\partial^2}{\partial R^2}\Phi_{\mu'}\right]+2\left[\Phi_\mu,\frac{\partial}{\partial R}\Phi_{\mu'}\right]\frac{d}{dR}\ , \tag{17}$$

and where the scalar products indicate five-dimensional integration over the Ω variables, i.e.,

$$(\Phi_\mu,A\Phi_\nu)=\int d\alpha d\hat{\mathbf{r}}_{12}d\hat{\mathbf{r}}_{12,3}(\sin^2\alpha)(\cos^2\alpha)\times\Phi_\mu^*(R;\Omega)A\Phi_\nu(R;\Omega)\ . \tag{18}$$

Practical applications of Macek's method,[1] thus far, have been restricted to obtaining and analyzing the solutions of Eq. (14), and then truncating the coupled system, Eq. (16), to a few dominant channels. Solving Eq. (14) is most difficult numerically for large values of R, where one may use instead the analytic expansion presented below.

B. $1/R$ perturbation series

We now proceed to cast the adiabatic (fixed R) equation, Eq. (14), into a form amenable to a perturbation series in $1/R$. This is possible only for wave functions localized near $\alpha=0$ (or $\pi/2$) at large R. For such states, $\langle\sin\alpha\rangle\to0$ as $R\to\infty$, such that the product $\langle R\sin\alpha\rangle$ tends to a constant value, independent of R. This suggests replacing α in the adiabatic equation by a new independent variable that is proportional to $R\sin\alpha$. This transformation is used below to construct the perturbation series. (States with energies above the threshold for three-body fragmentation oscillate throughout the range of α as $R\to\infty$ and are beyond the scope of our analysis.)

As $R\to\infty$, Eq. (14) should approach Schrödinger's equation for a pair of particles with relative coordinate $\mathbf{r}_{12}$, in the field of a third receding particle, at $|\mathbf{r}_{12,3}|\to\infty$. This becomes apparent upon performing a coordinate transformation $\alpha\to x$, where

$$x=\left[\frac{m}{m_{12}}\right]^{1/2}R\sin\alpha\ , \tag{19}$$

and where R is treated as a fixed parameter, such that

$$dx=\left[\frac{m}{m_{12}}\right]^{1/2}R(\cos\alpha)d\alpha\ . \tag{20}$$

This last equation renders the differential element $d\Omega$ in the form

$$d\Omega=(\sin^2\alpha)(\cos^2\alpha)d\alpha d\hat{\mathbf{r}}_{12}d\hat{\mathbf{r}}_{12,3}=\left[\frac{m_{12}}{mR^2}\right]^{3/2}\left[1-\frac{m_{12}x^2}{mR^2}\right]^{1/2}x^2dxd\hat{\mathbf{r}}_{12}d\hat{\mathbf{r}}_{12,3}\ . \tag{21}$$

The prefactor in Eq. (21) may be absorbed into the channel functions, setting

$$\Phi_\mu(R;\Omega)=\left[\frac{mR^2}{m_{12}}\right]^{3/4}\left[1-\frac{m_{12}x^2}{mR^2}\right]^{-1/4}\frac{\phi_\mu(R;\Omega)}{x}\ . \tag{22}$$

The combined transformations, Eqs. (19) and (22), applied to Eq. (14), yield

$$\left[-\frac{1}{2m_{12}}\left[\frac{\partial^2}{\partial x^2}-\frac{\mathbf{L}_{12}^2}{x^2}\right]+\frac{Z_1Z_2}{x}+V'(R,x,\theta)+\frac{1}{2mR^2}\left[x^2\frac{\partial^2}{\partial x^2}+2x\frac{\partial}{\partial x}+\frac{m_{12}x^2+4mR^2\mathbf{L}_{12,3}^2}{4(mR^2-m_{12}x^2)}+\frac{1}{2}\right]\right]\phi_\mu=U_\mu(R)\phi_\mu\ . \quad (23)$$

We emphasize that this equation is an exact form of the adiabatic equation, Eq. (14). Its solutions are to be normalized in accordance with the scalar product

$$\int_0^{x_{\max}}dx\int d\hat{\mathbf{r}}_{12}\int d\hat{\mathbf{r}}_{12,3}\phi_\mu^*(R;\Omega)\phi_\nu(R;\Omega)=\delta_{\mu,\nu}\ . \quad (24)$$

Note that the variable x, like the angle α, spans a finite range. From Eq. (19),

$$0\le x\le x_{\max}=\left[\frac{m}{m_{12}}\right]^{1/2}R\ . \quad (25)$$

As discussed below (see Sec. III A), the integral over x in Eq. (24) may be extended to $x_{\max}\to\infty$ if the channel functions ϕ_μ are localized at small values of x. This approximation excludes three-body fragmentation states and restricts the range of R over which our solutions to Eq. (23) are valid. The elimination of R from the limits of integration in Eq. (24) permits us to regard x (instead of α) as the independent variable, and to solve Eq. (23) by perturbation series in $1/R$.

The Hamiltonian operator for the isolated pair of particles $\{1,2\}$ is apparent in Eq. (23), and the Coulomb interactions of this pair with particle 3 are given by

$$V'(R,x,\theta)=\frac{Z_1Z_3\sqrt{m_{12,3}}}{|(mR^2-m_{12}x^2)^{1/2}\hat{\mathbf{r}}_{12,3}+[m_2\sqrt{m_{12,3}}/(m_1+m_2)]x\hat{\mathbf{r}}_{12}|}+\frac{Z_2Z_3\sqrt{m_{12,3}}}{|(mR^2-m_{12}x^2)^{1/2}\hat{\mathbf{r}}_{12,3}-[m_1\sqrt{m_{12,3}}/(m_1+m_2)]x\hat{\mathbf{r}}_{12}|}\ . \quad (26)$$

For fixed x values, each term of Eq. (26) is clearly proportional to $1/R$ as $R\to\infty$. The remaining contribution to Eq. (23) contains terms of order $(1/R)^2$ or higher.

It is now straightforward to expand each term in Eq. (23) in a power series in $1/R$. For the potential V' one obtains, to order $1/R^4$,

$$V'=\frac{\tilde{Z}}{\sqrt{m}R}+\frac{x\beta_1P_1(\cos\theta)}{mR^2}+\frac{m_{12}}{2}\frac{\tilde{Z}x^2}{(\sqrt{m}R)^3}+\frac{x^2\beta_2P_2(\cos\theta)}{(\sqrt{m}R)^3}+\frac{m_{12}x^3\beta_1P_1(\cos\theta)}{m^2R^4}+\frac{x^3\beta_3P_3(\cos\theta)}{m^2R^4}+\cdots\ , \quad (27)$$

where

$$\cos\theta=\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{12,3} \quad (28)$$

and

$$\tilde{Z}=\sqrt{m_{12,3}}Z_3(Z_1+Z_2)\ ,$$
$$\beta_1=\frac{m_3}{M}Z_3(m_1Z_2-m_2Z_1)\ ,$$
$$\beta_2=\left[\frac{m_3}{M}\right]^{3/2}\frac{Z_3(m_1^2Z_2+m_2^2Z_1)}{\sqrt{m_1+m_2}}\ , \quad (29)$$
$$\beta_3=\left[\frac{m_3}{M}\right]^2\frac{Z_3(m_1^3Z_2-m_2^3Z_1)}{m_1+m_2}\ .$$

Equation (27) results from the multipole expansion of Eq. (26) and is accordingly valid only over the restricted range

$$x<x_0=\frac{\sqrt{m}R}{\sqrt{m_{12}(1+m_3m_>/Mm_<)}}=\frac{x_{\max}}{\sqrt{1+m_3m_>/Mm_<}}\ , \quad (30)$$

with

$$m_>=\max(m_1,m_2)\ ,\quad m_<=\min(m_1,m_2)\ . \quad (31)$$

This places a more stringent restriction on the localization of the channel functions Φ_μ, as discussed in Sec. III A, below.

Writing Eq. (23) in the form

$$H(R)\phi_\mu(R;\Omega)=U_\mu(R)\phi_\mu(R;\Omega)\ , \quad (32)$$

and expanding the operator $H(R)$ in power series

$$H(R)=\sum_{j=0}^{\infty}\frac{1}{(\sqrt{m}R)^j}H_j\ , \quad (33)$$

we find for $j\le 4$

$$H_0=-\frac{1}{2m_{12}}\left[\frac{\partial^2}{\partial x^2}-\frac{\mathbf{L}_{12}^2}{x^2}\right]+\frac{Z_1Z_2}{x} ,$$
$$H_1=\tilde{Z} ,$$
$$H_2=\frac{1}{2}\left[x^2\frac{\partial^2}{\partial x^2}+2x\frac{\partial}{\partial x}+\frac{1}{2}+\mathbf{L}_{12,3}^2\right]$$
$$+x\beta_1P_1(\cos\theta) , \quad (34)$$
$$H_3=\frac{m_{12}}{2}\tilde{Z}x^2+x^2\beta_2P_2(\cos\theta) ,$$
$$H_4=\tfrac{1}{8}m_{12}x^2+\tfrac{1}{2}m_{12}x^2\mathbf{L}_{12,3}^2$$
$$+m_{12}x^3\beta_1P_1(\cos\theta)+x^3\beta_3P_3(\cos\theta) .$$

The channel functions and eigenvalues are also expanded in power series

$$\phi_\mu=\sum_{j=0}^{\infty}\frac{1}{(\sqrt{m}R)^j}\phi_\mu^{(j)} , \quad (35)$$

$$U_\mu=\sum_{j=0}^{\infty}\frac{1}{(\sqrt{m}R)^j}U_\mu^{(j)} . \quad (36)$$

Substituting Eqs. (33), (35), and (36) into Eq. (32) and comparing coefficients of equal powers of $1/R$, we obtain the indicial equation

$$H_0\phi_\mu^{(0)}=U_\mu^{(0)}\phi_\mu^{(0)} , \quad (37)$$

and the coupled set of inhomogeneous equations

$$(H_0-U_\mu^{(0)})\phi_\mu^{(j)}=\sum_{s=0}^{j-1}(U_\mu^{(j-s)}-H_{j-s})\phi_\mu^{(s)} ,$$
$$j=1,2,3,\ldots,\infty . \quad (38)$$

Note that Eqs. (34), (37), and (38) are independent of both R and m. Furthermore, the potential curves and channel functions, Eqs. (35) and (36), along with the prefactor in Eq. (22), depend only on the product $\sqrt{m}R$. We now proceed to solve this perturbation series to obtain the eigenvalues $U_\mu(R)$ to order $1/R^4$.

III. SOLUTIONS OF THE ASYMPTOTIC EQUATIONS

In this section, we solve Eqs. (37) and (38) in closed form to obtain the potentials $U_\mu^{(j)}$, $j\le 4$, and the wave functions $\phi_\mu^{(j)}$, $j\le 2$. That it is possible to obtain closed-form solutions stems from the fact that the response functions $\phi_\mu^{(j)}$ in Eq. (38) and the source terms $\phi_\mu^{(s)}$ $(s<j)$ share a common exponential dependence on x. Once this exponential is removed, Eq. (38) is reduced to a finite-order polynomial equation in x, which may be solved by expansion in Laguerre polynomials.

A. Indicial equation

Using the operator H_0 from Eq. (34), the indicial equation, Eq. (37), is written

$$\left[-\frac{1}{2m_{12}}\left[\frac{\partial^2}{\partial x^2}-\frac{\mathbf{L}_{12}^2}{x^2}\right]+\frac{Z_1Z_2}{x}\right]\phi_\mu^{(0)}=U_\mu^{(0)}\phi_\mu^{(0)} , \quad (39)$$

This equation is separable in the variables x and $\hat{\mathbf{r}}_{12}$. Its eigenvalues [recalling Eq. (1)] are

$$U_\mu^{(0)}=U_N^{(0)}=-\frac{m_{12}(Z_1Z_2)^2}{2N^2} , \quad (40)$$

and its degenerate eigenfunctions

$$\phi_\mu^{(0)}=\phi_{\nu,s}^{(0)}=\sum_{l=0}^{N-1}\ \sideset{}{'}\sum_{\lambda=|L-l|}^{L+l}A_{l,\lambda}^{\nu,s}R_{N,l}(\gamma x)Y_{l,\lambda}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3}) \quad (41)$$

are arbitrary superpositions of reduced Coulomb wave functions

$$R_{N,l}(\gamma x)=\eta_{Nl}(\gamma x)^{l+1}e^{-\gamma x/2}L_{N-l-1}^{2l+1}(\gamma x) , \quad (42)$$

where

$$\gamma=\frac{2m_{12}|Z_1Z_2|}{N} . \quad (43)$$

The function Y in Eq. (41) is a coupled product of spherical harmonics

$$Y_{l,\lambda}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})=\sum_{m_1,m_2}\langle lm_1\lambda m_2|LM\rangle$$
$$\times Y_{l,m_1}(\hat{\mathbf{r}}_{12})Y_{\lambda,m_2}(\hat{\mathbf{r}}_{12,3}) . \quad (44)$$

It is an eigenfunction of $\mathbf{L}^2$ and L_z, where $\mathbf{L}=\mathbf{L}_{12}+\mathbf{L}_{12,3}$ is the total orbital angular momentum about the center of mass. It is also a simultaneous eigenfunction of $\mathbf{L}_{12}^2$ and $\mathbf{L}_{12,3}^2$ with eigenvalues $l(l+1)$ and $\lambda(\lambda+1)$, respectively. We have introduced the notation $\mu=\{\nu,s\}$, where ν is the set of quantum numbers

$$\nu=\{N,L,M,\pi\} , \quad (45)$$

and s labels states of degenerate ν.

The coefficients A in Eq. (41) are undetermined to zeroth order in $1/R$. An eigenvalue equation which determines these coefficients is given in Sec. III C, below. Since $\phi_\mu^{(0)}$ must be an eigenfunction of parity (π), the sums over l and λ in Eq. (41) are restricted to even or odd combinations of $l+\lambda$. This is indicated by the prime over the second sum.

The normalization constant η_{Nl} of the reduced Coulomb wave function in Eq. (42) is determined as indicated by Eq. (24)

$$\int_0^\infty dx\,|R_{N,l}(\gamma x)|^2=1 \quad (46)$$

or

$$\eta_{Nl}^2=\frac{m_{12}|Z_1Z_2|(N-l-1)!}{N^2(N+l)!} . \quad (47)$$

In determining this factor, we have extended the range of integration in Eq. (24) to infinity. This is permissible due to the exponential attenuation of the solutions, Eq. (41), for x values greater than x_0 defined in Eq. (30). It does, however, place the following restriction on the range of validity of the asymptotic expansion:

$$\frac{(\gamma x_0)^{2N}e^{-\gamma x_0}}{2N(N+l)!(N-l-1)!} \ll 1, \quad x_0 > N/\gamma \; . \tag{48}$$

(Recall that x_0 depends only on R and on the masses, so that the left-hand side of this expression is a function of R.) The quantity on the left is a measure of the probability that $|\mathbf{r}_{12}|$ exceeds x_0. In practice, this restriction is of little consequence since one simply solves the exact adiabatic equation out to R values where a smooth match with this asymptotic expansion is obtained. Having stated this restriction, we will henceforth evaluate all scalar products over the extended range $0 \le x \le \infty$. The functions R_{Nl} then form a complete and orthonormal set, and we may proceed with the evaluation of higher-order terms.

Finally, we emphasize that the hyperspherical theory yields the correct fragmentation thresholds, given by Eq. (40). This is not true, for example, of the Born-Oppenheimer approximation, in which the potential curves approach energy levels with an incorrect reduced mass.[5]

B. First-order solutions

Using the results of Sec. III A, the first-order equation, Eq. (38) with $j=1$, is

$$(H_0 - U_n^{(0)})\phi_{\nu,s}^{(1)} = (U_{\nu,s}^{(1)} - \tilde{Z})\phi_{\nu,s}^{(0)} \; . \tag{49}$$

The left-hand side of this equation vanishes upon taking a scalar product with $\phi_{\nu,\sigma}^{(0)*}$, due to Eq. (39), and we find

$$U_{\nu,s}^{(1)} = \tilde{Z} \; , \tag{50}$$

where $\tilde{Z}$ is defined in Eq. (29). This is the expected result since the long-range potential now has the form

$$U_\mu(R) = -\frac{m_{12}(Z_1Z_2)^2}{2N^2} + \frac{\sqrt{m_{12,3}}(Z_1+Z_2)}{\sqrt{m}R} + O(1/R^2) \; , \tag{51}$$

and $\sqrt{m}R \simeq \sqrt{m_{12,3}}r_{12,3}$ in this limit. Note that the N-manifold states remain degenerate in this order of perturbation theory.

With the result, Eq. (50), Eq. (49) reduces to homogeneous form, and its solutions may be expressed as linear combinations of the degenerate zeroth-order solutions

$$\phi_{\nu,s}^{(1)} = \sum_\sigma a_\sigma^{\nu,s}\phi_{\nu,\sigma}^{(0)} \; , \tag{52}$$

where, like the A coefficients above, the $a_\sigma^{\nu,s}$ coefficients are undetermined to this order. These coefficients will be determined by the third-order equation in Sec. III D, below.

C. Second-order solutions

Selecting $j=2$ in Eq. (38), and using the results presented above, the second-order equation is

$$(H_0 - U_n^{(0)})\phi_{\nu,s}^{(2)} = (U_{\nu,s}^{(2)} - H_2)\phi_{\nu,s}^{(0)} \; . \tag{53}$$

Recall now that the $\phi_{\nu,s}^{(0)}$ driving term contained a set of undetermined coefficients due to the degeneracy of the N manifold at $R=\infty$. The first step in solving Eq. (53) is to determine these coefficients. Substituting Eq. (41) into Eq. (53), we find

$$(H_0 - U_N^{(0)})\phi_{\nu,s}^{(2)} = \sum_{l=0}^{N-1} \sideset{}{'}\sum_{\lambda=|L-l|}^{L+l} A_{l,\lambda}^{\nu,s}(U_{\nu,s}^{(2)} - H_2) \times R_{N,l}(\gamma x) Y_{l,\lambda}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3}) \; . \tag{54}$$

If we take the scalar product of Eq. (54) with $R_{N,l'}Y_{l',\lambda'}^{L,M*}$, then the left-hand side vanishes yielding

$$\sum_{l=0}^{N-1} \sideset{}{'}\sum_{\lambda=|L-l|}^{L+l} \langle Nl'\lambda' L|H_2|Nl\lambda L\rangle A_{l,\lambda}^{\nu,s} = U_{\nu,s}^{(2)} A_{l',\lambda'}^{\nu,s} \; , \tag{55}$$

which is a finite-dimensional eigenvalue equation determining the second-order potential $U_{\nu,s}^{(2)}/mR^2$ and the A coefficients introduced in Sec. III A.

The matrix elements of the operator H_2, within a degenerate N manifold, are obtained using the recurrence relations of the Laguerre polynomials. We find

$$\begin{aligned}\langle Nl'\lambda' L|H_2|Nl\lambda L\rangle = {} & \frac{\delta_{ll'}\delta_{\lambda\lambda'}}{2}\left[\lambda(\lambda+1) + \frac{l(l+1)}{2} - \frac{N^2}{2}\right] \\ & - \frac{3\beta_1}{\gamma}[\delta_{l',l-1}(N^2-l^2)^{1/2}\langle l-1,\lambda'|P_1(\cos\theta)|l,\lambda\rangle^L \\ & + \delta_{l',l+1}(N^2-(l+1)^2)^{1/2}\langle l+1,\lambda'|P_1(\cos\theta)|l,\lambda\rangle^L] \; ,\end{aligned} \tag{56}$$

where the angular factors are related to standard $3n-j$ symbols

$$\begin{aligned}\langle l',\lambda'|P_k(\cos\theta)|l,\lambda\rangle^L &= \int d\hat{\mathbf{r}}_{12} d\hat{\mathbf{r}}_{12,3} Y_{l'\lambda'}^{LM*}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3}) P_k(\cos\theta) Y_{l\lambda}^{LM}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3}) \\ &= (-1)^{\lambda+\lambda'+L}\sqrt{(2l+1)(2l'+1)(2\lambda+1)(2\lambda'+1)}\begin{Bmatrix} L & \lambda & l \\ k & l' & \lambda' \end{Bmatrix}\begin{pmatrix} l' & k & l \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} \lambda' & k & \lambda \\ 0 & 0 & 0 \end{pmatrix} \; .\end{aligned} \tag{57}$$

This angular factor, for $k=1$, vanishes unless $\lambda'=\lambda\pm1$.

For the special nondegenerate case $N=1$, Eq. (55) yields

$$U_{N=1}^{(2)}=\frac{L(L+1)}{2}-\frac{1}{4}\ , \tag{58}$$

and the adiabatic potential, through order $1/R^2$, is

$$U_\mu^{N=1}(R)=-\frac{m_{12}(z_1Z_2)^2}{2}+\frac{\sqrt{m_{12,3}}Z_3(Z_1+Z_2)}{\sqrt{m}R}+\frac{L(L+1)}{2mR^2}-\frac{1}{4mR^2}\ . \tag{59}$$

As shown in Ref. 1, the last term in Eq. (59) and the $1/4R^2$ term in Eq. (16) are canceled by the $1/R^2$ term in $W_\mu^\mu(R)$ (see Sec. III F, below).

Since Eq. (55) completes the determination of $\phi_{\nu,s}^{(0)}$ and $U_{\nu,s}^{(2)}$, we can now return to Eq. (53) and obtain the second-order wave functions $\phi_{\nu,s}^{(2)}$. Clearly, these can be determined only to within an arbitrary homogeneous contribution, which we write as

$$\phi_{\nu,s}^{(2)h}=\sum_\sigma b_\sigma^{\nu,s}\phi_{\nu,\sigma}^{(0)}\ . \tag{60}$$

The b coefficients will be determined by the fourth-order equation in Sec. III E, below,

The particular solutions of Eq. (53) might be obtained by expansion into zeroth-order functions $\phi_{\nu,\sigma}^{(0)}$ with alternative N values. This would clearly require the superposition of an infinite number of states, since, as was noted earlier, $\phi_{\nu,s}^{(2)}$ contains only that $e^{-\gamma x/2}$ factor which occurs in $\phi_{\nu,s}^{(0)}$. This suggests an alternative expansion into Sturmian functions

$$\begin{aligned}\phi_{\nu,s}^{(2)}&=\phi_{\nu,s}^{(2)h}+\phi_{\nu,s}^{(2)p}\ ,\\ \phi_{\nu,s}^{(2)p}&=\sum_{\substack{n\\ n\neq N}}\sum_{l=0}^{n-1}\sum_{\lambda=|L-l|}^{L+l}{}' T_{\nu,s}^{n,l,\lambda}S_{nl}(\gamma x)\\ &\quad\times Y_{l,\lambda}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})\ ,\end{aligned} \tag{61}$$

where γ is independent of n and is again given by Eq. (43) ($\gamma=2m_{12}|Z_1Z_2|/N$). We will show below that all but a few of the T coefficients in Eq. (61) vanish identically.

The Sturmian functions are defined by

$$S_{n,l}(\rho)=C_{nl}\rho^{l+1}e^{-\rho/2}L_{n-l-1}^{2l+1}(\rho)\ , \tag{62}$$

with

$$C_{nl}=\left[\frac{(n-l-1)!}{(n+l)!}\right]^{1/2}\ , \tag{63}$$

and are orthogonal with respect to the scalar product

$$\langle nl|n'l\rangle_S=\int_0^\infty\frac{d\rho}{\rho}S_{nl}^*(\rho)S_{n'l}(\rho)=\delta_{n,n'}\ . \tag{64}$$

Note that when $n=N$, the Sturmian functions are proportional to $R_{Nl}(\gamma x)$ of Eq. (42),

$$R_{Nl}(\gamma x)=\frac{\sqrt{m_{12}|Z_1Z_2|}}{N}S_{Nl}(\gamma x)\ , \tag{65}$$

and are accordingly also solutions of the homogeneous equation, Eq. (39). Thus the restriction to $n\neq N$ in Eq. (61).

The explicit form of Eq. (53) is

$$\begin{aligned}&\left[-\frac{1}{2m_{12}}\left[\frac{\partial^2}{\partial x^2}-\frac{\mathbf{L}_{12}^2}{x^2}\right]+\frac{Z_1Z_2}{x}+\frac{m_{12}(Z_1Z_2)^2}{2N^2}\right]\phi_{\nu,s}^{(2)}\\ &\quad=\left[U_{\nu,s}^{(2)}-\frac{1}{2}\left[x^2\frac{\partial^2}{\partial x^2}+2x\frac{\partial}{\partial x}+\frac{1}{2}+\mathbf{L}_{12,3}^2\right]-\beta_1xP_1(\cos\theta)\right]\phi_{\nu,s}^{(0)}\ .\end{aligned} \tag{66}$$

Setting

$$\rho=\gamma x\ , \tag{67}$$

and then left-multiplying Eq. (66) by ρ yields

$$\begin{aligned}&\frac{\gamma^2}{2m_{12}}\left[\left[-\rho\frac{\partial^2}{\partial\rho^2}+\frac{\mathbf{L}_{12}^2}{\rho}+\frac{\rho}{4}\right]-N\right]\phi_{\nu,s}^{(2)}\\ &\quad=\left[\rho U_{\nu,s}^{(2)}-\frac{1}{2}\left[\rho^3\frac{\partial^2}{\partial\rho^2}+2\rho^2\frac{\partial}{\partial\rho}+\frac{\rho}{2}+\rho\mathbf{L}_{12,3}^2\right]-\frac{\beta_1}{\gamma}\rho^2P_1(\cos\theta)\right]\phi_{\nu,s}^{(0)}\ .\end{aligned} \tag{68}$$

The operators in Eq. (68) are now Hermitian with respect to the Sturmian scalar product, Eq. (64). Note, in particular, that the Sturmian functions are solutions of the differential equation

$$\left[-\rho\frac{\partial^2}{\partial\rho^2}+\frac{l(l+1)}{\rho}+\frac{\rho}{4}\right]S_{nl}(\rho)=nS_{nl}(\rho)\ . \tag{69}$$

Upon substituting Eqs. (41) and (61) into Eq. (68), using Eqs. (65) and (69), and taking a Sturmian scalar product with $S_{nl}Y_{l\lambda}^{L,M*}$, we obtain

$$\begin{aligned}\left[\frac{N}{2}\right]^{1/2}\frac{\gamma^{3/2}}{m_{12}}(n-N)T_{\nu,s}^{n,l,\lambda}&=A_{l,\lambda}^{\nu,s}\left\langle nl\left|\left[U_{\nu,s}^{(2)}-\frac{l(l+1)}{2}-\frac{\lambda(\lambda+1)}{2}-\frac{1}{4}\right]\rho-\rho^2\frac{d}{d\rho}+\frac{N\rho^2}{2}-\frac{\rho^3}{8}\right|Nl\right\rangle_S\\ &\quad-\frac{\beta_1}{\gamma}\sum_{l'=0}^{N-1}\sum_{\lambda'=|L-l'|}^{L+l'}{}' A_{l',\lambda'}^{\nu,s}\langle nl|\rho^2|Nl'\rangle_S\langle l,\lambda|P_1(\cos\theta)|l',\lambda'\rangle^L\ .\end{aligned} \tag{70}$$

Equation (70) is the principal result of second-order perturbation theory. Since $n\neq N$, Eq. (70) uniquely determines the T coefficients in the expansion of the second-order wave function, Eq. (61). The matrix elements on the right-hand side of Eq. (70) may be evaluated using the recursion relations of the Laguerre polynomials. We find

$$T_{\nu,s}^{n,l,\lambda}=0, \quad |n-N|>3 \tag{71}$$

and the six non-vanishing coefficients

$$T_{\nu,s}^{N\pm 3,l,\lambda}=\pm\frac{1}{24}\left[\frac{2}{N}\right]^{1/2}\frac{m_{12}}{\gamma^{3/2}}A_{l,\lambda}^{\nu,s}V_{N,l}^{\pm}V_{N\pm 1,l}^{\pm}V_{N\pm 2,l}^{\pm} , \tag{72}$$

$$T_{\nu,s}^{N\pm 2,l,\lambda}=\mp\frac{m_{12}V_{N\pm 1,l}^{\pm}}{\sqrt{2N}\,\gamma^{3/2}}\left[A_{l,\lambda}^{\nu,s}\frac{(N\pm 1)}{4}V_{N,l}^{\pm}-\frac{\beta_1}{\gamma}(W_{N,l}^{\pm}G_{\lambda,l+1}^{\nu,s}+W_{N,l}^{\mp}G_{\lambda,l-1}^{\nu,s})\right] , \tag{73}$$

$$T_{\nu,s}^{N\pm 1,l,\lambda}=\mp\left[\frac{2}{N}\right]^{1/2}\frac{m_{12}}{\gamma^{3/2}}\left[A_{l,\lambda}^{\nu,s}V_{N,l}^{\pm}\left[U_{\nu,s}^{(2)}-\frac{\lambda(\lambda+1)}{2}-\frac{l(l+1)}{8}+\frac{N(N\pm 1)}{8}\right]\right.$$
$$\left.+\frac{2\beta_1}{\gamma}[(2N\pm l\pm 2)W_{N,l}^{\pm}G_{\lambda,l+1}^{\nu,s}+(2N\mp l\pm 1)W_{N,l}^{\mp}G_{\lambda,l-1}^{\nu,s}]\right] , \tag{74}$$

where the V and W factors are simply

$$V_{N,l}^{\pm}=\sqrt{(N\mp l)(N\pm l\pm 1)} ,$$
$$W_{N,l}^{\pm}=\sqrt{(N\mp l)(N\mp l\mp 1)} , \tag{75}$$

and

$$G_{\lambda,l\pm 1}^{\nu,s}=A_{l\pm 1,\lambda-1}^{\nu,s}\langle l,\lambda|P_1(\cos\theta)|l\pm 1,\lambda-1\rangle^L$$
$$+A_{l\pm 1,\lambda+1}^{\nu,s}\langle l,\lambda|P_1(\cos\theta)|l\pm 1,\lambda+1\rangle^L . \tag{76}$$

Note that the V and W factors cause the $T_{\nu,s}^{n,l,\lambda}$ coefficients to vanish unless $n\geq l+1$.

This completes the solution of the second-order equation. To summarize, the degeneracy of the zeroth-order solutions is split in second order by solving the finite-dimensional eigenvalue equation, Eq. (55). This determines the A coefficients for the zeroth-order wave functions, as well as the second-order potentials. The second-order wave functions are then given, to within an arbitrary homogeneous contribution, by the Sturmian expansion, Eq. (61), with coefficients given explicitly in Eqs. (71)–(76). We now proceed to third order.

D. Third-order solutions

In this section, we determine the third-order potential $U_{\nu,s}^{(3)}/(\sqrt{m}R)^3$. The first-order homogeneous contribution to the channel functions, Eq. (52), which was left undetermined in Sec. III B, is then given in explicit form.

Setting $j=3$ in Eq. (38) and using the above results

$$(H_0-U_N^{(0)})\phi_{\nu,s}^{(3)}=(U_{\nu,s}^{(3)}-H_3)\phi_{\nu,s}^{(0)}$$
$$+\sum_\sigma a_\sigma^{\nu,s}(U_{\nu,s}^{(2)}-H_2)\phi_{\nu,\sigma}^{(0)} . \tag{77}$$

Taking a scalar product with $\phi_{\nu,t}^{(0)*}$, the left-hand side vanishes and

$$U_{\nu,s}^{(3)}\delta_{s,t}=\langle\phi_{\nu,t}^{(0)}|H_3|\phi_{\nu,s}^{(0)}\rangle+a_t^{\nu,s}(U_{\nu,t}^{(2)}-U_{\nu,s}^{(2)}) . \tag{78}$$

Equation (78) is the principal result of third-order perturbation theory. When $s=t$, it yields directly the third-order potential

$$U_{\nu,s}^{(3)}=\langle\phi_{\nu,s}^{(0)}|H_3|\phi_{\nu,s}^{(0)}\rangle , \tag{79}$$

with H_3 given in Eq. (34). When $s\neq t$, Eq. (77) yields

$$a_t^{\nu,s}=\frac{\langle\phi_{\nu,t}^{(0)}|H_3|\phi_{\nu,s}^{(0)}\rangle}{U_{\nu,s}^{(2)}-U_{\nu,t}^{(2)}}, \quad s\neq t . \tag{80}$$

Note that the component $a_s^{\nu,s}$ cannot be determined by the third-order equation since its contribution to the channel function, Eq. (35), is equivalent to an R-dependent renormalization of the zeroth-order wave function. Instead, we note that the overlap integrals of the channel functions are now

$$\langle\phi_{\nu,s}|\phi_{\nu,s'}\rangle=\delta_{s,s'}+\frac{a_s^{\nu,s'}+a_{s'}^{\nu,s}}{\sqrt{m}R}+O\left[\frac{1}{R^2}\right] . \tag{81}$$

Orthonormality through first order then requires

$$a_{s'}^{\nu,s}=-a_s^{\nu,s'} , \tag{82}$$

which is clearly satisfied by the coefficients in Eq. (80), and which yields, for $s=s'$,

$$a_s^{\nu,s}=0 . \tag{83}$$

From the orthogonality of the Coulomb radial functions, one can now show that

$$\langle\phi_{\nu',s'}|\phi_{\nu,s}\rangle=\delta_{\nu,\nu'}\delta_{s,s'}+O\left[\frac{1}{R^2}\right] . \tag{84}$$

The matrix elements in Eqs. (79) and (80) can be evaluated using the recurrence relations of the Laguerre polynomials. We find

$$\langle\phi_{\nu t}^{(0)}|H_3|\phi_{\nu,s}^{(0)}\rangle=\frac{m_{12}\tilde{Z}(5N^2+1)}{\gamma^2}\delta_{s,t}-\frac{3m_{12}\tilde{Z}}{\gamma^2}\sum_{l=0}^{N-1}l(l+1)\sum_{\lambda=|L-l|}^{L+l}{}' A_{l,\lambda}^{\nu,t}A_{l,\lambda}^{\nu,s}$$
$$+\frac{2\beta_2}{\gamma^2}\sum_{l=0}^{N-1}\{[5N^2+1-3l(l+1)]M_{l,l}^{\nu,t,s}+5(W_{N-1,l}^{+}W_{N+1,l}^{-}M_{l,l+2}^{\nu,t,s}+W_{N+1,l}^{+}W_{N-1,l}^{-}M_{l,l-2}^{\nu,t,s})\} , \tag{85}$$

where the W factors were defined in Eq. (75), and where

$$M_{l,l'}^{\nu,t,s}=\sum_{\lambda=|L-l|}^{L+l}{}' A_{l,\lambda}^{\nu,t} \sum_{\lambda'=|L-l'|}^{L+l'}{}' A_{l',\lambda'}^{\nu,s}\langle l,\lambda|P_2(\cos\theta)|l',\lambda'\rangle^L . \tag{86}$$

We will not attempt, in this work, to obtain the third-order wave functions since the utility of our asymptotic expansion is anyway limited to large R by the constraint given in Eq. (48).

E. Fourth-order solutions

Setting $j=4$ in Eq. (38), and proceeding as in the previous section, we obtain the following expression for the fourth-order potential:

$$U_{\nu,s}^{(4)}=\langle \phi_{\nu,s}^{(0)}|H_4|\phi_{\nu,s}^{(0)}\rangle+\sum_{\sigma}(a_{\sigma}^{\nu,s})^2(U_{\nu,s}^{(2)}-U_{\nu,\sigma}^{(2)})-\frac{|Z_1Z_2|}{N}\sum_n (n-N)\sum_{l=0}^{n-1}\sum_{\lambda=|L-l|}^{L+l}{}' (T_{\nu,s}^{n,l,\lambda})^2 . \tag{87}$$

The coefficients of the homogeneous contribution to the second-order wave functions, Eq. (60), are then

$$b_t^{\nu,s}=-\langle \phi_{\nu,t}^{(0)}|\phi_{\nu,s}^{(2)p}\rangle+\frac{1}{U_{\nu,s}^{(2)}-U_{\nu,t}^{(2)}}\left[\langle \phi_{\nu,t}^{(0)}|H_4|\phi_{\nu,s}^{(0)}\rangle+a_t^{\nu,s}(U_{\nu,t}^{(3)}-U_{\nu,s}^{(3)})+\sum_{\sigma}a_{\sigma}^{\nu,s}a_{\sigma}^{\nu,t}(U_{\nu,t}^{(2)}-U_{\nu\sigma}^{(2)}) -\frac{|Z_1Z_2|}{N}\sum_n (n-N)\sum_{l=0}^{n-1}\sum_{\lambda=|L-l|}^{L+l}{}' T_{\nu,s}^{n,l,\lambda}T_{\nu,t}^{n,l,\lambda}\right] . \tag{88}$$

The evaluation of Eqs. (87) and (88) requires the matrix elements

$$\langle \phi_{\nu,t}^{(0)}|\phi_{\nu,s}^{(2)p}\rangle=-\frac{1}{2\sqrt{m_{12}|Z_1Z_2|}}\sum_{l=0}^{N-1}\sum_{\lambda=|L-l|}^{L+l}{}' A_{l,\lambda}^{\nu,t}(V_{N,l}^{+}T_{\nu,s}^{N+1,l,\lambda}+V_{N,l}^{-}T_{\nu,s}^{N-1,l,\lambda}) \tag{89}$$

and

$$\langle \phi_{\nu,t}^{(0)}|H_4|\phi_{\nu,s}^{(0)}\rangle=\frac{m_{12}}{4\gamma^2}\sum_{l,\lambda}A_{l,\lambda}^{\nu,t}A_{l,\lambda}^{\nu,s}[5N^2+1-3l(l+1)][1+4\lambda(\lambda+1)] +\frac{m_{12}}{2N\gamma^3}\sum_{l,\lambda}\sum_{l',\lambda'}A_{l,\lambda}^{\nu,t}A_{l',\lambda'}^{\nu,s}\left[\beta_1\langle l,\lambda|P_1|l',\lambda'\rangle^L+\frac{\beta_3}{m_{12}}\langle l,\lambda|P_3|l',\lambda'\rangle^L\right]\langle N,l|\rho^4|N,l'\rangle_S , \tag{90}$$

where

$$\langle N,l|\rho^4|N,l-3\rangle_S=-70N(N^2-l^2)^{1/2}\times[N^2-(l-1)^2]^{1/2}\times[N^2-(l-2)^2]^{1/2} ,$$
$$\langle N,l|\rho^4|N,l-1\rangle_S=-10N(N^2-l^2)^{1/2}\times(7N^2-3l^2+5) . \tag{91}$$

Note that Eq. (88) cannot be used to determine the coefficient $b_s^{\nu,s}$ since this contribution to the second-order wave function is equivalent to an R-dependent renormalization of the unperturbed function. Instead, the requirement of orthonormality

$$\langle \Phi_{\nu,s}|\Phi_{\nu,t}\rangle=\delta_{s,t}+O(1/R^3) \tag{92}$$

gives

$$b_s^{\nu,s}=-\langle \phi_{\nu,s}^{(0)}|\phi_{\nu,s}^{(2)p}\rangle-\tfrac{1}{2}\sum_{\sigma}(a_{\sigma}^{\nu,s})^2 . \tag{93}$$

These results complete the determination of the potential through fourth order in $1/R$, and of the channel functions through second order.

F. Derivative couplings

The coupling matrix elements $W_{\mu'}^{\mu}(R)$ in Eq. (17) can be obtained using the results in Secs. II A–III E, above. The general expressions are quite complicated in appearance, and only the most important elements, those diagonal in μ, are presented here.

Due to the orthogonality of the asymptotic wave functions, Eq. (92), the first derivative term vanishes identically

$$\left(\Phi_{\nu,s},\frac{\partial}{\partial R}\Phi_{\nu,s}\right)=0+O(1/R^4) . \tag{94}$$

The second derivative term contributes factors of second and higher orders and has the explicit form

$$\left[\Phi_{\nu,s},\frac{\partial^2}{\partial R^2}\Phi_{\nu,s}\right]=-\frac{2N^2+1}{4R^2}+\sum_{l,\lambda}\frac{l(l+1)}{2R^2}|A_{l,\lambda}^{\nu,s}|^2+\frac{2b_s^{\nu s}}{mR^4}$$
$$+\frac{1}{\sqrt{m}R^3}\sum_{l,\lambda}l(l+1)\left[A_{l,\lambda}^{\nu,s}\sum_\sigma\left[a_\sigma^{\nu,s}+\frac{1}{\sqrt{m}R}b_\sigma^{\nu,s}\right]A_{l,\lambda}^{\nu\sigma}+\frac{1}{2\sqrt{m}R}\left[\sum_\sigma a_\sigma^{\nu,s}A_{l,\lambda}^{\nu,\sigma}\right]^2\right]$$
$$+\frac{1}{mR^4}\sum_{\substack{n\\ n\neq N}}\sum_{l,\lambda}\frac{A_{l,\lambda}^{\nu,s}T_{\nu,s}^{n,l,\lambda}D_l^{n,N}}{4\sqrt{m_{12}|Z_1Z_2|}}+O(1/R^5)\,, \tag{95}$$

where the last term contains coefficients defined by

$$D_l^{N\pm1,N}=-[N^2+l(l+1)\mp 9N]V_{N,l}^{\pm}\,,$$
$$D_l^{N\pm2,N}=2(N\mp1)V_{N,l}^{\pm}V_{N\pm1,l}^{\pm}\,, \tag{96}$$
$$D_l^{N\pm3,N}=-V_{N,l}^{\pm}V_{N\pm1,l}^{\pm}V_{N\pm2,l}^{\pm}\,.$$

While the algebraic forms obtained throughout Sec. III appear formidable, they are amenable to rapid computation, and a Fortran program has been written for this purpose. In Sec. IV, some examples are presented to illustrate the use of these results, and to unravel the physical content of the algebraic forms.

IV. EXAMPLES AND DISCUSSION

In this section, the results of Sec. III are analyzed in detail for a few special cases. The algebraic formulas simplify considerably for the channel representing the particle pair (1,2) in its ground state $N=1$ and perturbed by the distant third particle. The results for this case are presented in Sec. IV A, below. Section IV B demonstrates that the asymptotic forms correctly contain a contribution due to the dipole polarizability of the hydrogen-like particle pair (1,2) in an arbitrary excited state N. Finally, Sec. IV C illustrates the numerical application of our results to a few systems of interest.

A. Ground-state channel

Consider the ground-state channel, for which the quantum numbers of Eq. (45) are

$$\nu=\{N=1,L,M,\pi=(-1)^L\},\quad s=1\,. \tag{97}$$

The eigenvalue problem, Eq. (55), is thus one dimensional, and

$$A_{l,\lambda}^{\nu,s}=\delta_{l,0}\delta_{\lambda,L}\delta_{s,1}\,. \tag{98}$$

The zeroth-order channel function is simply

$$\phi_{\nu,1}^{(0)}=R_{1,0}(\gamma x)Y_{0,L}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})\,, \tag{99}$$

and the first-order channel function is zero since, from Eq. (83),

$$a_1^{\nu,1}=0\,. \tag{100}$$

The G coefficients of Eq. (76) follow from Eq. (98)

$$G_{\lambda,l+1}^{\nu,1}=0,$$
$$G_{\lambda,l-1}^{\nu,1}=\frac{\delta_{l,1}}{\sqrt{3(2l+1)}}(\sqrt{L}\,\delta_{\lambda,L-1}-\sqrt{L+1}\delta_{\lambda,L+1})\,, \tag{101}$$

and the nonvanishing T coefficients of Eqs. (72)–(74) are

$$T_{\nu,1}^{4,0,L}=\frac{m_{12}}{(2\gamma^3)^{1/2}},\quad T_{\nu,1}^{3,1,L+1}=-\frac{2m_{12}\beta_1\sqrt{L+1}}{[(2L+1)\gamma^5]^{1/2}}\,,$$
$$T_{\nu,1}^{3,0,L}=-\frac{\sqrt{3}m_{12}}{(2\gamma^3)^{1/2}},\quad T_{\nu,1}^{2,1,L-1}=-\frac{8m_{12}\beta_1\sqrt{L}}{[(2L+1)\gamma^5]^{1/2}}\,, \tag{102}$$
$$T_{\nu,l}^{3,1,L-1}=\frac{2m_{12}\beta_1\sqrt{L}}{[(2L+1)\gamma^5]^{1/2}},\quad T_{\nu,1}^{2,1,L+1}=\frac{8m_{12}\beta_1\sqrt{L+1}}{[2L+1)\gamma^5]^{1/2}}\,.$$

The homogeneous contribution to the second-order wave function vanishes, since from Eq. (93)

$$b_1^{\nu,1}=0\,, \tag{103}$$

and the second-order wave function is then obtained from Eq. (61)

$$\phi_{\nu,1}^{(2)}=\frac{m_{12}xe^{-\gamma x/2}}{2\sqrt{2\gamma}}\left\{[L_3^1(\gamma x)-2L_2^1(\gamma x)]Y_{0,L}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})\right.$$
$$\left.+2\beta_1 x\frac{L_1^3(\gamma x)-8L_0^3(\gamma x)}{\sqrt{3(2L+1)}}[\sqrt{L}\,Y_{1,L-1}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})-\sqrt{L+1}\,Y_{1,L+1}^{L,M}(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{12,3})]\right\}\,. \tag{104}$$

The potential is now readily obtained from Eqs. (59), (79), and (87), and can be written in the form

$$U_{\nu,1}(R)=-\frac{m_{12}(Z_1Z_2)^2}{2}+\frac{\sqrt{m_{12,3}}Z_3(Z_1+Z_2)}{\sqrt{m}R}\left[1+\frac{6m_{12}}{mR^2\gamma^2}\right]-\frac{1}{4mR^2}$$
$$+\frac{L(L+1)}{2mR^2}\left[1+\frac{12m_{12}}{mR^2\gamma^2}\right]-\frac{3m_{12}}{4m^2R^4\gamma^2}\left[1+\frac{48\beta_1^2}{\gamma^2}\right]. \quad (105)$$

The diagonal coupling matrix, Eq. (95), is

$$W_{\nu,1}^{\nu,1}(R)=-\frac{3}{4R^2}\left[1+\frac{4m_{12}}{\gamma^2mR^2}\right]. \quad (106)$$

Combining these two forms, the effective potential which enters the coupled radial equations, Eq. (16), is

$$U_{\text{eff}}(R)=U_{\nu,1}(R)-\frac{1}{2m}\left[W_{\nu,1}^{\nu,1}(R)+\frac{1}{4R^2}\right]$$
$$=-\frac{m_{12}(Z_1Z_2)^2}{2}+\frac{\sqrt{m_{12,3}}Z_3(Z_1+Z_2)}{\sqrt{m}R}\left[1+\frac{6m_{12}}{mR^2\gamma^2}\right]$$
$$+\frac{L(L+1)}{2mR^2}\left[1+\frac{12m_{12}}{mR^2\gamma^2}\right]+\frac{3m_{12}}{4\gamma^2m^2R^4}\left[1-\frac{48\beta_1^2}{\gamma^2}\right]+O(1/R^5), \quad (107)$$

where for $N=1$, $\gamma=2m_{12}|Z_1Z_2|$.

Each term in Eq. (107) may be interpreted by comparison with the close-coupling form of the asymptotic potential. Denoting zeroth-order expectation values by, for example,

$$\langle r_{12}^2\rangle_0=\langle\phi_{\nu,1}^{(0)}|r_{12}^2|\phi_{\nu,1}^{(0)}\rangle=\frac{12}{\gamma^2}, \quad (108)$$

it follows that

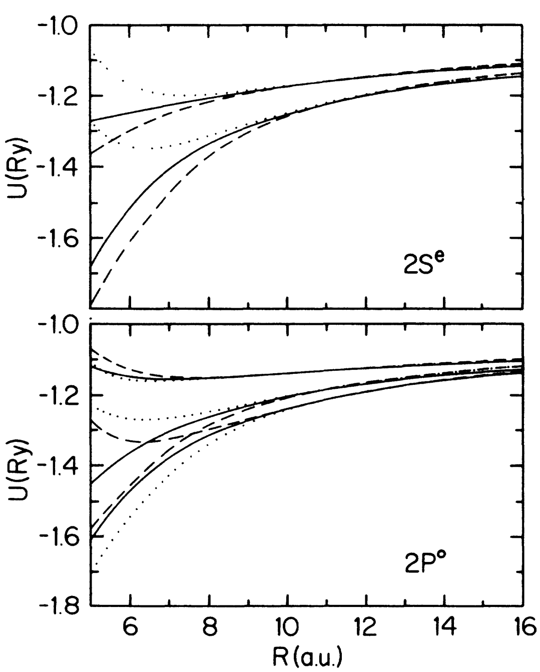

FIG. 1. Comparison of our analytical potential curves to numerical solutions of the adiabatic equation for $2S^e$ and $2P^o$ doubly excited channels of He. Solid lines, our results. Dashed and dotted lines are the numerical results for singlet and triplet states, respectively. We have chosen $m=1$.

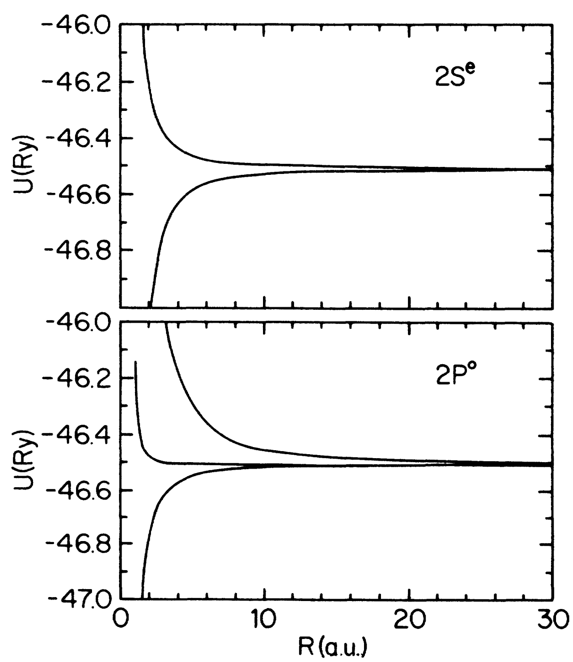

FIG. 2. Long-range potential curves for the $2S^e$ and $2P^o$ channels of the $(p^+\mu^-)e^-$ system.

$$\left\langle \frac{1}{\sqrt{m_{12,3}}r_{12,3}} \right\rangle_0 = \frac{1}{\sqrt{m}R}\left[1+\frac{6m_{12}}{mR^2\gamma^2}\right]+O(1/R^5)\,,$$
$$\left\langle \frac{1}{m_{12,3}r_{12,3}^2} \right\rangle_0 = \frac{1}{mR^2}\left[1+\frac{12m_{12}}{mR^2\gamma^2}\right]+O(1/R^6)\,,\qquad (109)$$
$$\left\langle \frac{1}{m_{12,3}^2r_{12,3}^4} \right\rangle_0 = \frac{1}{m^2R^4}+O(1/R^6)\,.$$

The effective potential can now be written in the form

$$U_{\rm eff}(R) = -\frac{m_{12}(Z_1Z_2)^2}{2}+\left\langle\frac{Z_3(Z_1+Z_2)}{r_{12,3}}\right\rangle_0 +\left\langle\frac{L(L+1)}{2m_{12,3}r_{12,3}^2}\right\rangle_0 - \frac{\alpha_1}{2}\left\langle\frac{Z_3^2}{r_{12,3}^4}\right\rangle_0 +\frac{m_{12}}{16m_{12,3}^2}\left\langle\frac{r_{12}^2}{r_{12,3}^4}\right\rangle_0 \qquad (110)$$

where the dipole polarizability of the $N=1$ state is

$$\alpha_1=\frac{9(m_1Z_2-m_2Z_1)^2}{2m_{12}^3(m_1+m_2)^2|Z_1Z_2|^4}\,, \qquad (111)$$

and is precisely the form given in standard references.[12] The final term in Eq. (110) opposes the attractive dipole polarizability, and is the only term in the expansion of the $N=1$ channel that is unique to the hyperspherical theory. Its contribution can be traced to he $m_{12}x^2/8$ term in H_4 of Eq. (34).

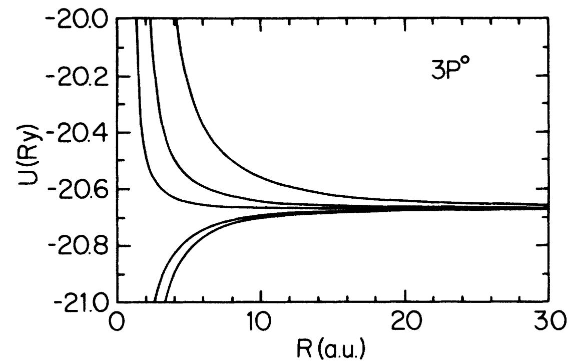

FIG. 3. Same as Fig. 2 for $N=3$, $L=1$, and odd parity.

B. Excited-state dipole polarizability

The presence of a dipole-polarization term in $U_{\rm eff}$ also holds for higher N manifolds. To see this, note that this factor originates from the β_1^2 contribution to the T^2 term in the fourth-order energy, Eq. (87). This contribution can be extracted directly using Eq. (70), and results in the general form

$$\alpha_{\nu,s}=\frac{N^3(m_1Z_2-m_2Z_1)^2}{8m_{12}^3(m_1+m_2)^2|Z_1Z_2|^4}\sum_{n\neq N}\sum_{l,\lambda}\frac{|\sum_{l',\lambda'}A_{l',\lambda'}^{\nu,s}\langle n,l|\rho^2|N,l'\rangle_S\langle l,\lambda|P_1|l',\lambda'\rangle^L|^2}{n-N}\,. \qquad (112)$$

Note that the form of this expression is typical of a second-order energy correction. The matrix elements needed for its evaluation are

$$\langle N\pm1,l|\rho^2|N,l-1\rangle_S=2[2N\mp(l-1)]W_{N,l}^{\mp}\,,$$
$$\langle N\pm1,l|\rho^2|N,l+1\rangle_S=2[2N\pm(l+2)]W_{N,l}^{\pm}\,,\qquad (113)$$
$$\langle N\pm2,l|\rho^2|N,l=1\rangle_S=-W_{N,l}^{\mp}V_{N\pm1,l}^{\pm}\,,$$
$$\langle N\pm2,l|\rho^2|N,l+1\rangle_S=-W_{N,l}^{\pm}V_{N\pm1,l}^{\pm}\,.$$

C. Numerical results

Figure 1 compares our results for $N=2$ channels of atomic He with those obtained by numerically diagonalizing the adiabatic Hamiltonian. The basis used for the diagonalization was the same as that used in Ref. 2, and was truncated to the harmonic quantum number $\lambda=120$. For $\sqrt{m}R$ greater than 10 (a.u.), where the singlet and triplet channels merge, our analytic results match the numerical ones quite well. Our method cannot, of course, include the exchange symmetry. Recently, a numerical procedure has been developed to incorporate the exchange symmetry in the asymptotic region.[13]

Figures 2 and 3 show the potential curves of $2S^e$, $2P^o$, and $3P^o$ channels for the $(p\mu)e$ system. The bound p-μ system, in its low-lying excited states, has a small dipole moment. Consequently, the curves are flat over a large range of $\sqrt{m}R$ and diverge rapidly at small distances. This system, in which the two heavy particles are oppositely charged, is one of the least studied three-body problems. Its high-N channels are of particular interest, for they constitute the final states of muon-capture processes in atomic hydrogen. The calculation of small-R potential curves for this system is presently under investigation.

D. Conclusions

We have developed a systematic asymptotic expansion for the two-body fragmentation channels of three-body systems. Our method applies quite generally to any three-body system which interacts via Coulomb forces. The wave functions obtained are polarized orbitals which incorporate the dominant polarization energy as well as corrections due to our choice of reaction coordinate.

ACKNOWLEDGMENTS

One of us (M.C.) thanks Anthony Starace for his assistance, and acknowledges the support of the U.S. Department of Energy, Division of Chemical Sciences, under Grant No. DE-FG02-85ER13955. Z.Z. and J.M. wish to acknowledge sponsorship by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Grant No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

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