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Orbital-Angular-Momentum Decomposition of the Three-Body Coupling Scheme: Muonic Molecules and the Hydrogen Molecular Ion

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In obtaining the wave functions of three-body Coulomb systems in which two heavy equally charged, and one light oppositely charged, particles are involved, one can use a type of Born-Oppenheimer coupling scheme, to obtain nonadiabatic effects. In this paper we decompose the coupled differential equations of such a scheme in terms of the total orbital angular momentum and parity of the states, and reduce these equations to one-dimensional ones in a form suitable for calculation.

I. INTRODUCTION

Much work has been done in evaluating the bound states of three-body systems involving two heavy equally charged particles, and one light oppositely charged particle.[1] Generally, the situations of interest are those in which the heavy particles are the proton, deuteron, and triton in various combinations, and the light particle is either an electron or negative muon. In the electron case adiabatic-type approximations give accurate results for systems such as the hydrogen molecular ion, because of the small electron-proton mass ratio. The dynamical effects of the protons can then be obtained by means of a type of Born-Oppenheimer expansion.[2]

In the muon case, the states of interest have been either $L=0$, muonic molecules, $(p\mu d)^+$, $(p\mu t)^+$, etc., for nuclear catalysis[3] and nuclear-potential studies,[4] or $L=1$ muonic molecules, $(p\mu p)^+$, for muon capture[5] and proton-structure studies,[6] where L is the total orbital angular momentum of the system. Because of the size of the muon-proton mass ratio, the most accurate μ-molecular wave functions have been obtained by variational means[7] rather than by the use of Born-Oppenheimer schemes, which couple the various adiabatic solutions via the nuclear motion terms in the Hamiltonian. Nonetheless, some calculations using these coupling techniques have been performed by Cohen, Judd, and Riddell[8] (CJR).

More recently, some interest has been shown in excited states of muonic molecules,[9] and estimates of the energies of such states have been made. The dynamical couplings of such states, and hence their true angular momentum symmetries have not, however, been taken into account. In addition, recent interest in highly accurate values for the hydrogen-molecular-ion energy spectrum has led to calculations using a scheme similar to that of Ref. 8, in an attempt to get accurate contributions to the energy from higher electronic orbitals.[10] That work, however, only considers couplings to states of the same azimuthal quantum numbers, i.e., σ states among themselves, or π states among themselves (where σ and π are the azimuthal quantum numbers of the "two-fixed-center" solutions), whereas if one takes into account the full angular momentum symmetry of the states one gets σ, π mixing for $L=1$ states, etc.

In order to fully appreciate the dynamical coupling scheme approach to these and other problems it is useful to fully explore the restrictions imposed on the coupled equations by angular momentum and parity symmetries in a very general way. In this paper we extract the most general information possible based on these symmetries, and finally end up with coupled equations in only one variable, the interheavy particle distance, for any given total orbital angular momentum, L and parity P. These equations then exhibit explicitly the relation between similar states of different L and P, as well as putting the equations in a form suitable for straightforward numerical calculations.

In Sec. II we discuss the separations of the Hamiltonian and the resulting coupled differential equations. In Sec. III some symmetry properties are discussed, in Sec. IV the coupling matrix is actually evaluated, and in Sec. V the general form of the coupled differential equations is determined, and some general conclusions are drawn.

II. COUPLING SCHEME

The coupling scheme developed here is very similar to those of CJR[8] and Hunter, Gray, and Pritchard.[10] The main difference is that the muon coordinate r_μ is here measured from the geometric center of the two-nuclear line rather than from its center of mass. This has the advantage of separating the coupling terms into those with the same, and those with opposite parity under $\vec{r}_\mu \to -\vec{r}_\mu$. The total Hamiltonian for the three-body system is

$$H=\frac{-\hbar^2}{2M_1}\nabla_{R_1}{}^2-\frac{\hbar^2}{2M_2}\nabla_{R_2}{}^2-\frac{\hbar^2}{2m_\mu}\nabla_{R_\mu}{}^2 + e^2/r_{12}-e^2/r_{1\mu}-e^2/r_{2\mu}\ , \qquad (1)$$

where $\vec{R}_1$, $\vec{R}_2$, and $\vec{R}_\mu$ are the position vectors of the two heavy particles (M_1 and M_2) and of the light particle (m_μ) (muon or electron), respectively. r_{12}, $r_{1\mu}$, $r_{2\mu}$ are the interparticle distances. Let

$$\vec{R}=\frac{M_1\vec{R}_1+M_2\vec{R}_2+m_\mu\vec{R}_\mu}{\alpha}\ , \quad \alpha\equiv M_1+M_2+m_\mu\ , \qquad (2)$$

$$\vec{r}_n=\vec{R}_2-\vec{R}_1\ , \quad \vec{r}_\mu=\vec{R}_\mu-\tfrac{1}{2}(\vec{R}_1+\vec{R}_2)\ .$$

Then (1) becomes

$$H=\frac{-\hbar^2}{2\alpha}\nabla_R{}^2-\frac{\hbar^2}{2M_r}\nabla_{r_n}{}^2\frac{-\hbar^2}{2\overline{m}_\mu}\nabla_{r_\mu}{}^2-\frac{\hbar^2}{2\overline{M}}\vec{\nabla}_{r_n}\cdot\vec{\nabla}_{r_\mu} + e^2/r_n-e^2/r_{1\mu}-e^2/r_{2\mu}\ , \qquad (3)$$

$$M_r\equiv\frac{M_1M_2}{M_1+M_2}\ , \quad \overline{m}_\mu\equiv\frac{4M_r m_\mu}{4M_r+m_\mu}\ , \quad \overline{M}\equiv\frac{M_1M_2}{M_2-M_1}\ .$$

Eliminating the center-of-mass motion we have left

$$H'\Psi=E\Psi\ ,$$

$$H'=\frac{-\hbar^2}{2M_r}\nabla_{r_n}{}^2-\frac{\hbar^2}{2\overline{m}_\mu}\nabla_{r_\mu}{}^2-\frac{\hbar^2}{2\overline{M}}\vec{\nabla}_{r_n}\cdot\vec{\nabla}_{r_\mu} + e^2/r_n-e^2/r_{1\mu}-e^2/r_{2\mu}\ . \qquad (4)$$

Letting $\overline{R}_\mu\equiv e^4\overline{m}_\mu/2\hbar^2$, $\overline{A}_\mu=\hbar^2/\overline{m}_\mu e^2$,

$$\overline{\epsilon}\equiv 4m_\mu/(4M_r+m_\mu),\quad \delta\equiv(M_2-M_1)/(M_2+M_1),$$

and $\vec{r}_n\to A_\mu\vec{r}_n$, $\vec{r}_\mu\to\overline{A}_\mu\vec{r}_\mu$, $E\to\overline{R}_\mu E$, (5)

we get for (4)

$$[-\overline{\epsilon}\nabla_{r_n}{}^2-\nabla_{r_\mu}{}^2-\overline{\epsilon}\delta\vec{\nabla}_{r_n}\cdot\vec{\nabla}_{r_\mu} + 2/r_n-2/r_{1\mu}-2/r_{2\mu}]\Psi=E\Psi\ . \qquad (6)$$

In the special case of identical particles ($M_1=M_2$) we get (a) $\overline{\epsilon}\to 2m''_\mu/M$ (where M is heavy mass, and m''_μ is muon mass reduced with respect to combined mass of identical particles). (b) $\delta=0$. We now extract the two-fixed-center Hamiltonian from (6) and let

$$H'_\mu\equiv-\nabla_{r_\mu}{}^2-\frac{2}{r_{1\mu}}-\frac{2}{r_{2\mu}}\ , \quad H'_\mu\psi_i=W_i(r_n)\psi_i\ . \qquad (7)$$

Then the exact solution of (6) can be written

$$\Psi=\textstyle\sum_i\chi_i(\vec{r}_n)\psi_i(r_n,\vec{r}_\mu)\ . \qquad (8)$$

We note that ψ_i depends on $\vec{r}_\mu$, and on the magnitude of $\vec{r}_n$. We now choose polar coordinates to describe the vectors $\vec{r}_n,\vec{r}_\mu$, where r_n,θ_r,ϕ_r are the magnitude, polar, and azimuthal angles of $\vec{r}_n$ in some fixed frame of reference. r_μ,θ,ϕ are the magnitude, polar, and azimuthal angles of $\vec{r}_\mu$ in a frame of reference whose z axis is along $\vec{r}_n$, and whose x axis lies in the plane of $\vec{r}_n$ and the z axis of the fixed frame. Hence, θ is the angle between $\vec{r}_n$ and $\vec{r}_\mu$, and ϕ is the angle between the planes formed by $\vec{r}_n$ and the fixed z axis, and the three-particle configuration, respectively. Then the total wave function can be written

$$\Psi=\Psi(\theta_r,\phi_r,\phi;r_n,r_\mu,\theta)\ , \qquad (9a)$$

where θ_r,ϕ_r,ϕ are the euler angles of the three-body system, and r_n,r_μ,θ describe the internal configuration. The dependence of Ψ on θ_r,ϕ_r,ϕ is determined completely by the angular momentum symmetry of the state (see below). The problem is hence reducible to that of solving for the r_n,r_μ,θ dependence. In terms of r_n,θ_r,ϕ_r, the two-fixed-center solutions are of the form

$$\psi_i(r_n,\vec{r}_\mu)=\psi_i(\phi;r_n,r_\mu,\theta) \qquad (9b)$$

and the nuclear part is of the form

$$\chi_i(\vec{r}_n)=\chi_i(\theta_r,\phi_r,r_n)\ . \qquad (9c)$$

It is precisely this splitting of the euler angles between the ψ_i and χ_i that obscures the angular momentum symmetry in the coupling scheme. The ψ_i have been obtained in exact form by Bates, Ledsham, and Stewart[11] and are characterized by three quantum numbers n,l,m:

$$m=0,1,2,\ldots \quad l=0,1,2,\ldots \quad n=1,2,\ldots \qquad (10a)$$
$$\sigma,\pi,\Delta,\ldots \qquad s,p,d,\ldots .$$

m is the azimuthal quantum number in the two-fixed-center system and corresponds to the exactly conserved z component of angular momentum for that system. l corresponds, in the limit of small r_n, to the total angular momentum quantum number, and n is the principle quantum number. In general

$$\psi_i=k_{nlm}(r_n,r_\mu,\theta)\{\cos m\phi,\ \sin m\phi\}, \qquad (10b)$$

with energy $W_{nlm}(r_n)$. Even l states are even under $P_\mu(\vec{r}\to-\vec{r}_\mu)$ and are labeled g states. Odd l states are odd under P_μ and are labeled u states. Typical states are then written $1s\sigma g$, $2s\sigma g$, $2p\sigma u$, $2p\pi u$, $3d\sigma g$, etc., each state being doubly degenerate, having either $\cos m\phi$ or $\sin m\phi$ dependence.

We now proceed to the coupling scheme. Substituting (8) into (6), multiplying on the left by ψ_j^* and integrating over $\vec{r}_\mu$ ($\vec{r}_n$ fixed) we obtain (following CJR[8])

$$-\bar{\epsilon}\sum_i \int \psi_j^* \nabla_{r_n}{}^2(\chi_i\psi_i)\,d^3r_\mu$$
$$-\bar{\epsilon}\,\delta\sum_i \int \psi_j^* \nabla_{r_n}\cdot\nabla_{r_\mu}(\chi_i\psi_i)\,d^3r_\mu$$
$$+[W_j(r_n)+2/r_n]\chi_j = E\chi_j\ . \tag{11}$$

After several integration by parts and rearrangements we get

$$[-\bar{\epsilon}\nabla_{r_n}{}^2 + W_j(r_n)+2/r_n]\,\chi_j$$
$$-\bar{\epsilon}\sum_i \Theta_{ji}\chi_i - \bar{\epsilon}\,\delta\sum_k \tilde{\Theta}_{jk}\chi_k = E\chi_j\ , \tag{12a}$$

where
$$\Theta_{ji} = 2\vec{f}_{ji}\cdot\vec{\nabla}_{r_n} + (\vec{\nabla}_{r_n}\cdot\vec{f}_{ji}) - g_{ji}\ , \tag{12b}$$
$$\tilde{\Theta}_{ji} = \tilde{\vec{f}}_{ji}\cdot\vec{\nabla}_{r_n} + (\vec{\nabla}_{r_n}\cdot\tilde{\vec{f}}_{ji}) - \tilde{g}_{ji}\ ,$$

and
$$\vec{f}_{ji} = \int \psi_j^*\vec{\nabla}_{r_n}\psi_i\,d^3r_\mu = -\vec{f}_{ij}\ ,$$
$$g_{ji} = \int \vec{\nabla}_{r_n}\psi_j^*\cdot\vec{\nabla}_{r_n}\psi_i\,d^3r_\mu = g_{ij}\ ,$$
$$\tilde{\vec{f}}_{ji} = \int \psi_j^*\,\vec{\nabla}_{r_\mu}\psi_i\,d^3r_\mu\ , \tag{12c}$$
$$\tilde{g}_{ji} = \int \vec{\nabla}_{r_n}\psi_j^*\cdot\vec{\nabla}_{r_\mu}\psi_i\,d^3r_\mu\ .$$

We note that to evaluate the Θ_{ji}, $\tilde{\Theta}_{ji}$, two differential operators are involved: $\vec{\nabla}_{r_n}$ and $\vec{\nabla}_{r_\mu}$. $\vec{\nabla}_{r_n}$ means differentiate holding r_μ fixed, $\vec{\nabla}_{r_\mu}$ means differentiate holding $\vec{r}_n$ fixed. In terms of our variables $(\theta_r, \phi_r, \phi; r_n, r_\mu, \theta)$ and unit vectors $\hat{r}_n, \hat{\theta}_r, \hat{\phi}_r$, we get

$$\vec{\nabla}_{r_n} = \hat{r}_n\frac{\partial}{\partial r_n} + \frac{\hat{\theta}_r}{r_n}\left\{\frac{\partial}{\partial\theta_r} - \cos\phi\frac{\partial}{\partial\theta} + \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right\}$$
$$+\frac{\hat{\phi}_r}{r_n\sin\theta_r}\left\{\frac{\partial}{\partial\phi_r} - \sin\theta_r\sin\phi\frac{\partial}{\partial\theta}\right.$$
$$\left.-[\cot\theta\cos\phi\sin\theta_r + \cos\theta_r]\frac{\partial}{\partial\phi}\right\}, \tag{13a}$$

$$\vec{\nabla}_{r_\mu} = \hat{r}_n\left\{\cos\theta\frac{\partial}{\partial r_\mu} - \frac{\sin\theta}{r_\mu}\frac{\partial}{\partial\theta}\right\}$$
$$+\hat{\theta}_r\left\{\sin\theta\cos\phi\frac{\partial}{\partial r_\mu} + \frac{\cos\theta\cos\phi}{r_\mu}\frac{\partial}{\partial\theta}\right.$$
$$\left.-\frac{\sin\phi}{r_\mu\sin\theta}\frac{\partial}{\partial\phi}\right\} + \hat{\phi}_r\left\{\sin\theta\sin\phi\frac{\partial}{\partial r_\mu}\right.$$
$$\left.+\frac{\cos\theta\sin\phi}{r_\mu}\frac{\partial}{\partial\theta} + \frac{\cos\phi}{r_\mu\sin\theta}\frac{\partial}{\partial\phi}\right\}\ . \tag{13b}$$

Under P_μ ($\vec{r}_\mu\to-\vec{r}_\mu$, $\vec{r}_n$ unchanged; i.e., $\theta\to\pi-\theta$, $\phi\to\pi+\phi$) none of the components of $\vec{\nabla}_{r_n}$ change the sign. Thus, $\vec{\nabla}_{r_n}\psi_i$ has the same P_μ symmetry as ψ_i. Examining Eq. (12b) and (12c) we see that $\Theta_{ji}=0$ unless ψ_j and ψ_i have the same P_μ symmetry. Similarly, under P_μ each component of $\vec{\nabla}_{r_\mu}$ changes sign. Hence, $\nabla_{r_\mu}\psi_i$ has opposite P_μ symmetry to ψ_i. Looking again at (12b) and (12c), we have $\tilde{\Theta}_{ji}=0$ unless ψ_j and ψ_i have the opposite P_μ symmetry. Thus, for identical particles ($\delta=0$) only like-muon-parity states are coupled.

III. SOME SYMMETRY CONSIDERATIONS

As we saw in Sec. II the total three-body wave function could be written $\Psi(\theta_r, \phi_r, \phi; r_n, r_\mu, \theta)$, where θ_r, ϕ_r, ϕ describe the external configuration of the three-body system. If we consider a state of definite total orbital angular momentum $L^2 = l(l+1)$, then the L_z components of Ψ at different external configurations are related by the irreducible representations of the rotation group. In Wigner's notation[12]

$$\Psi^l_{\mu'}(\theta_r, \phi_r, \phi; r_n, r_\mu, \theta)$$
$$=\sum_{\mu=-l}^{l}(-1)^{\mu'-\mu}D^l(\phi_r, \theta_r, \phi)_{\mu'\mu}\overline{\Psi}_\mu(r_n, r_\mu, \theta). \tag{14}$$

The $\overline{\Psi}_\mu(r_n, r_\mu, \theta)$ are $(2l+1)$ internal configuration wave functions, which if known give us the entire wave function. It is sufficient for our purposes to restrict ourselves to $\Psi(L=1, L_z=0)$, i.e., to $\mu'=0$ in (14). (This eliminates the variable ϕ_r from consideration.)

We now look at some special cases of (14). First we define total parity

$$P_T:\ (\vec{r}_n\to-\vec{r}_n; \vec{r}_\mu\to-\vec{r}_\mu)\quad \text{or: } \theta\to\theta,\ \phi\to\pi-\phi,\ \theta_r\to\pi-\theta_r,\ \phi_r\to\pi+\phi_r,$$

and muon parity, as before,

$$P_\mu:\ (\vec{r}_n \to \vec{r}_n; \vec{r}_\mu \to -\vec{r}_\mu) \qquad \text{or: } \theta \to \pi - \theta,\ \phi \to \pi + \phi,\ \theta_r \to \theta_r,\ \phi_r \to \phi_r\,. \tag{15}$$

We note that the total Hamiltonian (4) conserves P_T, and in the special case of identical particles, P_μ. (We note further that $P_\mu \times \text{exchange} = P_T$).

Case (i) $L=0$:

$$\Psi = \Psi(r_n, r_\mu, \theta), \quad \text{only even } P_T \text{ exist.} \tag{16}$$

Since there is no ϕ dependence, only σ states in (8) can contribute, and hence in (12a) only σ-type terms are coupled. If in addition the heavy particles are identical, only σg or σu-type terms are coupled.

Case (ii) $L=1$, $L_z=0$ [from (14)]:

$$\Psi_0 = -(\sin\theta_r/\sqrt{2})\, e^{-i\phi}\bar{\Psi}_{-1} + \cos\theta_r \bar{\Psi}_0 + (\sin\theta_r/\sqrt{2})\, e^{+i\phi}\bar{\Psi}_{+1}\,,$$

and for different P_T

$$\Psi(L=1, L_z=0, \text{ even } P_T) = g_1 \sin\theta_r \sin\phi,$$

$$\Psi(L=1, L_z=0, \text{ odd } P_T) = f_2 \cos\theta_r + g_2 \sin\theta_r \cos\phi, \tag{17}$$

where g_1, f_2, g_2 are functions of (r_n, r_μ, θ). Here clearly one gets (σ,π) coupling as well as (σ,σ) and (π,π) coupling for odd P_T, but only (π,π) coupling for even P_T. For the case of identical particles we again get only even or odd P_μ states coupling. The even or oddness puts restrictions on g_1, f_2, g_2

Even P_μ	Odd P_μ
g_1 odd under P_μ,	g_1 even under P_μ,
f_2 even, g_2 odd	f_2 odd, g_2 even .

Similarly for $L=2$, $L_z=0$: Case (iii):

$$\Psi(L=2, L_z=0, \text{ even } P_T) = \tfrac{1}{2} f_1 (3\cos^2\theta_r - 1) + g_1 \cos\theta_r \sin\theta_r \cos\phi + h_1 \sin^2\theta_r \cos 2\phi\,,$$

$$\Psi(L=2, L_z=0, \text{ odd } P_T) = g_2 \cos\theta_r \sin\theta_r \sin\phi + h_2 \sin^2\theta_r \sin 2\phi\,. \tag{18}$$

Here clearly σ, π, Δ are coupled for even P_T; π, Δ for odd P_T. For identical particle case we again have only even or odd P_μ terms coupled and again

P_μ even	P_μ odd
f_1 even under P_μ,	f_1 odd under P_μ,
g_1 odd, h_1 even,	g_1 even, h_1 odd,
g_2 odd, h_2 even .	g_2 even, h_2 odd .

We now write the general form of Ψ for arbitrary L, obtainable from (14) (with a slight change of notation).

$$\Psi[L=l, L_z=0, P_T=(-1)^l] = \sum_{i=0}^{l} f_i^{(1)}(r_n, r_\mu, \theta) P_l^i(\cos\theta_r)\cos i\phi\,,$$

$$\Psi[L=l, L_z=0, P_T=(-1)^{l+1}] = \sum_{i=1}^{l} f_i^{(2)}(r_n, r_\mu, \theta) P_l^i(\cos\theta_r)\sin i\phi\,. \tag{19}$$

As in the special cases we note that only ψ_i appear in (8) for which the azimuthal quantum number "m" runs from 0 to l and from 1 to l, respectively. Furthermore, we can also see that only $\cos m\phi$ or $\sin m\phi$ terms appear, and hence there is no coupling between cosine- and sine-type two-fixed-center orbitals in Eqs. (12). The $P_l^i(\cos\theta_r)$ are the usual associated Legendre Polynomials and the $f_i^{1,2}(r_n, r_\mu, \theta)$ are internal wave functions. For the identical particle case, we have

P_μ even:

$$f_i^{(1)} \to (-1)^i f_i^{(1)}; \quad f_i^{(2)} \to (-1)^i f_i^{(2)}\,,$$

P_μ odd:

$$f_i^{(1)} \to (-1)^{i+1} f_i^{(1)}; \quad f_i^{(2)} \to (-1)^{i+1} f_i^{(2)}\,, \tag{20}$$

under $P_\mu(\theta \to \pi - \theta)$. One important point about the above coupling conditions should be mentioned. Whereas the $\cos i\phi$, $\sin j\phi$ (all i- and j-type) terms in (8) do not couple because Θ_{ij}, $\tilde{\Theta}_{ij}$ vanish for those terms, and whereas the even and odd P_μ states do not couple for the identical particle case because the coefficient of $\tilde{\Theta}_{ij}$ vanishes, the fact that only the first $l+1$ azimuthal, two-fixed-center states appear in a given $L=l$ solution, comes not from the vanishing of the Θ_{ij} but from the fact that such a choice forms a self-consistent set of solutions of the coupled equations (12a) (see Sec. IV). That the above symmetry considerations are indeed consistent with Eq. (12a) can be seen by explicit construction of the matrix elements.

IV. COUPLING MATRIX

Let the two-fixed-center solution,[13]

$$\psi_{nlm}(r_n, \vec{r}_\mu) \equiv k_{nlm}(r_n, r_\mu, \theta)\{\cos m\phi,\ \sin m\phi\},$$

be written $M_i\{\cos m\phi,\ \sin m\phi\}$, where the index i corresponds to the pair (n, l); M corresponds to m. (21)

The form CM_i and SM_i will be used as indices to indicate states of the $\cos m\phi$ and $\sin m\phi$ type, respectively. (We note that CM_i states are defined for $m \geq 0$; SM_i states for $m \geq 1$). Hence, Θ_{CM_i, SN_j} means that the left-hand-side function in (12c) is $M_i \cos m\phi$ and the right-hand-side function is $N_j \sin n\phi$.[j] By use of (13a) and (13b) in (12c) and by integrating over ϕ, we can evaluate the $\mathfrak{f}_{ji}, g_{ji}$, and $\tilde{\mathfrak{f}}_{ji}, \tilde{g}_{ji}$. These are evaluated in Appendix A. For $L_z = 0$ states the Θ_{ij} and $\tilde{\Theta}_{ij}$ then have the following properties:

$$\Theta_{CM_i, SN_j} = \tilde{\Theta}_{CM_i, SN_j} = \text{transposes} = 0, \quad \text{all } M_i, N_j \tag{22a}$$

$$\Theta_{CM_i, CN_j} = \Theta_{SM_i, SN_j}\ ;\ \tilde{\Theta}_{CM_i, CN_j} = \tilde{\Theta}_{SM_i, SN_j}, \tag{22b}$$

all M_i, N_j for which SM_i, SN_j are defined.

$$\Theta_{CM_i, CN_j} = \tilde{\Theta}_{CM_i, CN_j} = 0, \quad \text{unless} \quad n = \{m-1,\ m,\ m+1\}. \tag{22c}$$

For the nonzero elements we have (dropping the C and S coefficients)

$$\Theta_{M_i, [M+1]_j} = \frac{-1}{r_n^2}\{a(M_i, [M+1]_j) + (m+1) b(M_i, [M+1]_j)\}\left\{\frac{\partial}{\partial\theta_r} + (m+1)\cot\theta_r\right\}, \tag{23a}$$

$$\Theta_{M_i, M_j} = 2c(M_i, M_j)\frac{\partial}{\partial r_n} + \frac{2c(M_i, M_j)}{r_n} + \frac{dc(M_i, M_j)}{dr_n} - d(M_i, M_j)$$

$$- \frac{1}{r_n^2}[e(M_i, M_j) + m^2 f(M_i, M_j)] - m^2 \delta_{ij}\frac{\cot^2\theta_r}{r_n^2}, \tag{23b}$$

$$\Theta_{M_i, [M-1]_j} = \frac{-1}{r_n^2}\{a(M_i, [M-1]_j) - (m-1) b(M_i, [M-1]_j)\}\left\{\frac{\partial}{\partial\theta_r} - (m-1)\cot\theta_r\right\}. \tag{23c}$$

Similarly,

$$\tilde{\Theta}_{M_i, [M+1]_j} = \frac{1}{2r_n}\{\tilde{a}(M_i, [M+1]_j) + (m+1)\tilde{b}(M_i, [M+1]_j)\}\left\{\frac{\partial}{\partial\theta_r} + (m+1)\cot\theta_r\right\}. \tag{24a}$$

$$\tilde{\Theta}_{M_i, M_j} = \tilde{c}(M_i, M_j)\frac{\partial}{\partial r_n} + \frac{2}{r_n}\tilde{c}(M_i, M_j) + \frac{d\tilde{c}(M_i, M_j)}{dr_n} - \tilde{d}(M_i, M_j) + \frac{1}{r_n}[\tilde{e}(M_i, M_j) + m^2 \tilde{f}(M_i, M_j)]. \tag{24b}$$

$$\tilde{\Theta}_{M_i, [M-1]_j} = \frac{1}{2r_n}\{\tilde{a}(M_i, [M-1]_j) - (m-1)\tilde{b}(M_i, [M-1]_j)\}\left\{\frac{\partial}{\partial\theta_r} - (m-1)\cot\theta_r\right\}. \tag{24c}$$

(It is understood that in addition to the above; Θ couples only M_i, N_j states with the same P_μ symmetry, and $\tilde{\Theta}$ couples only M_i, N_j states of opposite P_μ symmetry). The $a(M_i, N_j), \ldots, f(M_i, N_j)$ and $\tilde{a}(M_i, N_j), \ldots, \tilde{f}(M_i, N_j)$ are simple integral (over $\vec{r}_\mu$ space) functionals of the ordered pairs of states M_i, N_j, and hence are functions of only one variable r_n. They are tabulated in Appendixes A and B.[14] We are now in a position to obtain the coupled equations (12a) for a given total orbital angular momentum $L = l$, $(L_z = 0)$ and either parity P_T.

V. FINAL COUPLED EQUATIONS

The total solution for $L=l, L_z=0$, and the two P_T values can now be written in the form (8) using the information of Eq. (19).

$$\Psi[L=l, L_z=0, P_T=(-1)^l] = \sum_{m=0}^{\infty} \sum_{\text{all allowed } i} \chi_{M_i}^{(1)}(r_n, \theta_r) M_i(r_n, r_\mu, \Theta)\cos m\phi\ , \tag{25a}$$

$$\Psi[L=l, L_z=0, P_T=(-1)^{l+1}] = \sum_{m=1}^{\infty} \sum_{\text{all allowed } i} \chi_{M_i}^{(2)}(r_n, \theta_r) M_i(r_n, r_\mu, \theta)\sin m\phi\ . \tag{25b}$$

In addition, from Eq. (19) we must have

$$\chi_{M_i}(r_n, \theta_r) = \overline{\chi}_{M_i}(r_n) P_l^m(\cos\theta_r), \quad m \leq l; \quad \chi_{M_i}(r_n, \theta_r) = 0, \quad m > l\ . \tag{26}$$

A. Equal Mass Case (Identical Particles)

In terms of the properties of the Θ and $\tilde{\Theta}$ (12a) can be written as follows, using (23a)–(23c):

$$\Big\{ -\overline{\epsilon}\frac{1}{r_n^2}\frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} - \frac{\overline{\epsilon}}{r_n^2}\left[\frac{1}{\sin\theta_r}\frac{\partial}{\partial\theta_r}\sin\theta_r\frac{\partial}{\partial\theta_r} - \frac{m^2}{\sin^2\theta_r} + m^2\right] + W_i(r_n) + \frac{2}{r_n}$$
$$+ \overline{\epsilon}\left[d(M_i, M_i) + \frac{e(M_i, M_i)}{r_n^2} + m^2\frac{f(M_i, M_i)}{r_n^2}\right]\Big\}\chi_{M_i} - \overline{\epsilon}\sum_{j\neq i}\Theta_{M_i M_j}\chi_{M_j}$$
$$+ \frac{\overline{\epsilon}}{r_n^2}\sum_j\{a(M_i, [M-1]_j) - (m-1)b(M_i, [M-1]_j)\}\left\{\frac{\partial}{\partial\theta_r} - (m-1)\cot\theta_r\right\}\chi_{[M-1]_j}$$
$$+ \frac{\overline{\epsilon}}{r_n^2}\sum_j\{a(M_i, [M+1]_j) + (m+1)b(M_i, [M+1]_j)\}\left\{\frac{\partial}{\partial\theta_r} + (m+1)\cot\theta_r\right\}\chi_{[M+1]_j} = E\chi_{M_i}\ . \tag{27}$$

The second term in the first curly brackets contains the angular part of $\nabla_{r_n}^2$ and the θ_r-dependent part of the self-coupling term Θ_{M_i, M_i}. Hence, all the θ_r dependence of the coupled equations are explicitly expressed in (27). The smallest m value of interest is 0 for solution (25a), and 1 for solution (25b).
We note that

$$\left[\frac{1}{\sin\theta_r}\frac{\partial}{\partial\theta_r}\sin\theta_r\frac{\partial}{\partial\theta_r} - \frac{m^2}{\sin^2\theta_r} + m^2\right]P_l^m(\cos\theta_r) = -[l(l+1) - m^2]P_l^m(\cos\theta_r)\ ,$$
$$\left[\frac{\partial}{\partial\theta_r} - (m-1)\cot\theta_r\right]P_l^{m-1}(\cos\theta_r) = -P_l^m(\cos\theta_r)\ , \tag{28}$$
$$\left[\frac{\partial}{\partial\theta_r} + (m+1)\cot\theta_r\right]P_l^{m+1}(\cos\theta_r) = (l-m)(l+m+1)P_l^m(\cos\theta_r)\ .$$

Substituting (26) into (27) and using (28) we see that we indeed have a consistent set of equations – as we must. Canceling out the θ_r dependence we get for the $(l+1)$ types of equation corresponding to different m values $[P_T = (-1)^l$ state$]$

0th: $$\left\{-\overline{\epsilon}\frac{1}{r_n^2}\frac{\partial}{\partial r_n}r_n^2\frac{\partial}{\partial r_n} + \frac{\overline{\epsilon}\, l(l+1)}{r_n^2} + W_{\sigma_i}(r_n) + \frac{2}{r_n} + \overline{\epsilon}\left[d(\sigma_i, \sigma_i) + \frac{1}{r_n^2}e(\sigma_i, \sigma_i)\right]\right\}\overline{\chi}_{\sigma_i}$$
$$-\overline{\epsilon}\sum_{j\neq i}\Theta_{\sigma_i\sigma_j}\overline{\chi}_{\sigma_j} + \frac{\overline{\epsilon}\, l(l+1)}{r_n^2}\sum_j\{a(\sigma_i, \pi_j) + b(\sigma_i, \pi_j)\}\overline{\chi}_{\pi_j} = E\overline{\chi}_{\sigma_i}\ ,$$

where $M_i \to \sigma_i (m=0)$, $\pi_i (m=1)$, $\Delta_i (m=2)$, etc.

$$mth:\quad \left\{-\bar{\epsilon}\frac{1}{r_n^2}\frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} + \frac{\bar{\epsilon}[l(l+1)-m^2]}{r_n^2} + W_{M_i}(r_n) + \frac{2}{r_n} + \bar{\epsilon}\left[d(M_i,M_i) + \frac{e(M_i,M_i)}{r_n^2} + \frac{m^2 f(M_i,M_i)}{r_n^2}\right]\right\}\bar{\chi}_{M_i}$$

$$-\bar{\epsilon}\sum_{j\neq i}\Theta_{M_iM_j}\bar{\chi}_{M_j} - \frac{\bar{\epsilon}}{r_n^2}\sum_j\{a(M_i,[m-1]_j) - (m-1)b(M_i,[M-1]_j)\}\bar{\chi}_{[M-1]_j}$$

$$+[\bar{\epsilon}(l-m)(l+m+1)/r_n^2]\sum_j\{a(M_i,[M+1]_j) + (m+1)b(M_i,[M+1]_j)\}\bar{\chi}_{[M+1]_j} = E\bar{\chi}_{M_i}\ ,$$

$$lth:\quad \left\{-\bar{\epsilon}\frac{1}{r_n^2}\frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} + \frac{\bar{\epsilon}l}{r_n^2} + W_{l_i}(r_n) + \frac{2}{r_n} + \bar{\epsilon}\left[d(L_i,L_i) + \frac{e(L_i,L_i)}{r_n^2} + \frac{l^2 f(L_i,L_i)}{r_n^2}\right]\right\}\bar{\chi}_{L_i}$$

$$-\bar{\epsilon}\sum_{j\neq i}\Theta_{L_iL_j}\bar{\chi}_{L_j} - \frac{\bar{\epsilon}}{r_n^2}\sum_j\{a(L_i,[L-1]_j) - (l-1)b(L_i,[L-1]_j)\}\bar{\chi}_{[L-1]_j} = E\bar{\chi}_{L_i}\ , \tag{29}$$

where the indices i,j refer to either even P_μ or odd P_μ states. The solution for $P_T = (-1)^{l+1}$ is obtained by setting $\bar{\chi}_{\sigma_i} = 0$ all i, in Eq. (29).

B. Unequal Mass Case

We note that $\tilde{\Theta}_{M,[M-1]}$, $\tilde{\Theta}_{M,[M+1]}$ have the same general form as the $\Theta_{M,[M-1]}$, $\Theta_{M,[M+1]}$ terms. Furthermore, $\tilde{\Theta}_{M,M}$ has no θ_r dependence. We now let the indices i and j refer to even P_μ states, and the indices r and s refer to odd P_μ states. (For visualization purposes a superscript ± will also be put on even and odd P_μ terms.) Again looking at the solution $P_T = (-1)^l$ and noting that the $P_T = (-1)^{l+1}$ solution obeys the same equations with $\bar{\chi}_{\sigma_i} = \bar{\chi}_{\sigma_r} = 0$ all i and r, we have for m^+-type equations with $0 \leq m \leq l$:

$$\left\{-\bar{\epsilon}\frac{1}{r_n^2}\frac{\partial}{\partial r_n} r_n^2 \frac{\partial}{\partial r_n} + \frac{\bar{\epsilon}[l(l+1)-m^2]}{r_n^2} + W^+_{M_i}(r_n) + \frac{2}{r_n} + \bar{\epsilon}\left[d(M_i,M_i) + \frac{e(M_i,M_i)}{r_n^2} + \frac{m^2 f(M_i,M_i)}{r_n^2}\right]\right\}\bar{\chi}^+_{M_i}$$

$$-\bar{\epsilon}\sum_{j\neq i}\Theta_{M_iM_j}\bar{\chi}^+_{M_j} - \frac{\bar{\epsilon}}{r_n^2}\sum_j\{a(M_i,[M-1]_j) - (m-1)b(M_i,[M-1]_j)\}\bar{\chi}^+_{[M-1]_j}$$

$$+[\bar{\epsilon}(l-m)(l+m+1)/r_n^2]\sum_j\{a(M_i,[M+1]_j) + (m+1)b(M_i,[M+1]_j)\}\bar{\chi}^+_{[M+1]_j}$$

$$-\bar{\epsilon}\delta\sum_s\tilde{\Theta}_{M_iM_s}\bar{\chi}^-_{M_s} + (\bar{\epsilon}\delta/2r_n)\sum_s\{\tilde{a}(M_i,[M-1]_s) - (m-1)\tilde{b}(M_i,[M-1]_s)\}\bar{\chi}^-_{[M-1]_s}$$

$$-[\bar{\epsilon}\delta(l-m)(l+m+1)/2r_n]\sum_s\{\tilde{a}(M_i,[M+1]_s) + (m+1)\tilde{b}(M_i,[M+1]_s)\}\bar{\chi}^-_{[M+1]_s} = E\bar{\chi}^+_{M_i}\ . \tag{30}$$

For the m^- equation the result is the same as above if we let $i\to r$, $j\to s$, and $r\to i$, $s\to j$, and (+) superscript $\to$ (−).

VI. DISCUSSION

It should be noted that the spin-orbit coupling of the electron (muon) has been completely neglected here. This corresponds to Hunds case B[15] of angular momentum coupling in molecules. This neglect of the spin-orbit force in the coupled equations will put significant limits on a highly accurate calculation of electronic admixtures only for cases where the state is not predominantly σ-type. In the σ-type states, which are the ones where accuracy is needed for both the muonic molecules[16] and the hydrogen molecular ions, only the small π state admixture in $L=1$ states couples the spin to the orbit, and the spin-orbit interaction can be dealt with via perturbation theory.

The coupled equations (29) and (30) exhibit various well-known molecular phenomena. If we assume $\bar{\epsilon}$ is small and restrict ourselves to an approximate solution of the form $\chi_{M_i}\psi_{M_i}$,[17] ignoring coupling to other electronic states, then the nuclear wave function χ_{M_i} satisfies an equation where the main rotational energy term is $\bar{\epsilon}[l(l+1)-m^2]/r_n^2$, which corresponds to the energy of the symmetric top with angular momentum m about the symmetry axis. The main "effective-potential" term for the vibrational levels is $[W_{M_i}(r_n)+2/r_n]$. The self-coupling terms

$$\bar{\epsilon}[d(M_i,M_i)+e(M_i,M_i)/r_n^{\,2}+m^2 f(M_i,M_i)/r_n^{\,2}]$$

represent the modification of the rotational energy associated with the fact that the molecule is not rigid, and the modification of the nuclear potential due to dynamical effects; i.e., it represents the coupling of the rotational and vibrational motion to the electronic motion. If we include the coupling to other electronic orbitals we get a splitting of the two degenerate opposite P_T states: CM_i and SM_i, since only CM_i couples to σ states.

In a recent calculation Carter,[9] restricting himself to an adiabatic approximation, demonstrated the existence of $L=1(2p\pi u)$ μ-molecular bound states. In calculating the energies of the two levels he assumes that the opposite parity potentials have different centrifugal terms: 0 and $2\bar{\epsilon}/r_n^2$ corresponding to relative angular momenta of the nuclei 0, 1. The exact form of the coupled equations (29) and (30) for case $m=1$ indicates immediately that the centrifugal term is the same for both parity states, and that the energy splitting arises from the σ coupling of the odd-parity state, and hence is of order $(\bar{\epsilon})^2$. Work is presently underway to obtain more accurate values for these excited muonic molecules.

Work is also presently underway to use the coupled equations to calculate the effect of the π-state admixture on the various levels of the hydrogen molecular ion, carrying the results of Hunter *et al.*[10] one step further. In addition, an attempt will be made to obtain accurate $L=0$, $L=1$ μ-molecular wave functions (σ type) by coupling as many electron states as are available. By observing the rate of convergence of the energy as more orbitals are included, one could hope to get a more definitive statement about the energy of those states than via the variational procedure; and a more suitable form of wave function for subsequent use. This technique will only work if the convergence rate is sufficient, and if the contribution of the continuum two-fixed-center states is small.

APPENDIX A

To evaluate the Θ_{ij} and $\tilde{\Theta}_{ij}$ coupling matrices we note that, using Eq. (13), the following integrals appear in (12c) for the $\vec{f}_{ij}, g_{ij}; \vec{\tilde{f}}_{ij}, \tilde{g}_{ij}$:

$$\int_0^{2\pi} \cos m\phi \cos n\phi \cos\phi \, d\phi = (\pi/2)\{\delta_{m,n-1}+\delta_{m,n+1}+\delta_{m+n,1}\} \equiv \pi\Delta^1_{m,n},$$

$$\int_0^{2\pi} \cos m\phi \sin n\phi \sin\phi \, d\phi = (\pi/2)\{\delta_{m,n-1}-\delta_{m,n+1}+\delta_{m+n,1}\} \equiv \pi\Delta^2_{m,n},$$

$$\int_0^{2\pi} \sin m\phi \sin n\phi \cos\phi \, d\phi = (\pi/2)\{\delta_{m,n-1}+\delta_{m,n+1}-\delta_{m+n,1}\} \equiv \pi\Delta^3_{m,n}, \qquad \text{(A1)}$$

$$\int_0^{2\pi} \begin{Bmatrix}\cos m\phi \cos n\phi \\ \sin m\phi \sin n\phi\end{Bmatrix} \sin\phi \, d\phi = \int^{2\pi} \cos m\phi \sin n\phi \cos\phi \, d\phi = 0 \, .$$

We let $\bar{\delta}_{m,n} \equiv \delta_{m,n}+\delta_{0m}\delta_{0n}$, and write $\pi = \int_0^{2\pi} \cos^2\phi \, d\phi$. (A2)

Then
$$\vec{f}_{CM_i,CN_j} = \hat{r}_n c'(M_i,N_j)\bar{\delta}_{m,n} + (\hat{\theta}_r/r_n)[-a'(M_i,N_j)\Delta^1_{m,n} - nb'(M_i,N_j)\Delta^2_{n,m}] \, ,$$

$$\vec{f}_{SM_i,SN_j} = \hat{r}_n c'(M_i,N_j)\delta_{m,n} + (\hat{\theta}_r/r_n)[-a'(M_i,N_j)\Delta^3_{m,n} + nb'(M_i,N_j)\Delta^2_{m,n}] \, ,$$

$$\vec{f}_{CM_i,SN_j} = (\hat{\phi}_r/r_n)[-a'(M_i,N_j)\Delta^2_{m,n} - nb'(M_i,N_j)\Delta^1_{m,n}] - (\hat{\phi}_r \cot\theta_r/r_n)[n\delta_{ij}\delta_{m,n}] \, ,$$

$$g_{CM_i,CN_j} = d'(M_i,N_j)\bar{\delta}_{m,n} + (1/r_n^{\,2})[e'(M_i,N_j) + mnf'(M_i,N_j)]\,\bar{\delta}_{m,n} \qquad \text{(A3)}$$

$$+\frac{\cot^2\theta_r}{r_n^2}[mn\delta_{ij}\delta_{m,n}]+\frac{\cot\theta_r}{r_n^{\,2}}[-na'(N_j,M_i)\Delta^2_{m,n}-ma'(M_i,N_j)\Delta^2_{n,m}+2mnb'(M_i,N_j)\Delta^3_{m,n}]\,,$$

$$g_{CM_i,SN_j}=0\,.$$

$$g_{SM_i,SN_j}=d'(M_i,N_j)\delta_{m,n}+\frac{1}{r_n^{\,2}}[e'(M_i,N_j)+mnf'(M_i,N_j)]\,\delta_{m,n}+\frac{\cot^2\theta_r}{r_n^{\,2}}[mn\delta_{ij}\delta_{m,n}]$$

$$+\frac{\cot\theta_r}{r_n^{\,2}}[na'(N_j,M_i)\Delta^2_{n,m}+ma'(M_i,N_j)\Delta^2_{m,n}+2mnb'(M_i,N_j)\Delta^1_{m,n}]\,,$$

where, $a'(M_i,N_j)=\int M_i\,\frac{\partial N_j}{\partial\theta}\cos^2\phi\,d^3r_\mu\,,\quad b'(M_i,N_j)=\int M_i\,N_j\cot\theta\cos^2\phi\,d^3r_\mu\,,$

$$c'(M_i,N_j)=\int M_i\,\frac{\partial N_j}{\partial r_n}\cos^2\phi\,d^3r_\mu\,,\quad d'(M_i,N_j)=\int\frac{\partial M_i}{\partial r_n}\,\frac{\partial N_j}{\partial r_n}\cos^2\phi\,d^3r_\mu\,, \tag{A4}$$

$$e'(M_i,N_j)=\int\frac{\partial M_i}{\partial\theta}\,\frac{\partial N_j}{\partial\theta}\cos^2\phi\,d^3r_\mu,\quad f'(M_i,N_j)=\int M_iN_j\cot^2\theta\cos^2\phi\,d^3r_\mu\,.$$

Note that for $m,n\geq 1$ we have $\Delta^1_{m,n}=\Delta^3_{m,n}$ and $\Delta^2_{m,n}=-\Delta^2_{n,m}$, and that SM_i is defined only for $m\geq 1$; therefore we get

$$\vec{\mathrm{f}}_{CM_i,CN_j}=\vec{\mathrm{f}}_{SM_i,SN_j}\,;\quad g_{CM_i,CN_j}=g_{SM_i,SN_j}\,. \tag{A5}$$

Note that $\vec{\mathrm{f}}_{CM_i,SN_j}$ has no ϕ_r dependence, and that we are dealing with $L_z=0$ states only; therefore we have from (12b)

$$\Theta_{CM_i,SN_j}=\Theta_{SM_i,CN_j}=0\,. \tag{A6}$$

Equations (23) follow from (A3)–(A6), where

$$a(M_i,N_j)=a'(M_i,N_j),\ldots,f(M_i,N_j)=f'(M_i,N_j),\quad\text{for } m\geq 1,\ \ n\geq 1\,;$$
$$a(M_i,N_j)=2a'(M_i,N_j),\ldots,f(M_i,N_j)=2f'(M_i,N_j),\quad\text{for } m \text{ and/or } n=0\,.$$

Similarly $(CM_i\to m\geq 0; SM_i\to m\geq 1)$

$$\vec{\tilde{\mathrm{f}}}_{CM_i,CN_j}=\vec{\tilde{\mathrm{f}}}_{SM_i,SN_j}=\hat{r}_n\tilde{c}'(M_i,N_j)\bar{\delta}_{m,n}+\hat{\theta}_r[\tilde{a}'(M_i,N_j)\Delta^1_{m,n}+n\tilde{b}'(M_i,N_j)\Delta^2_{m,n}],$$

$$\vec{\tilde{\mathrm{f}}}_{CM_i,SN_j}=\hat{\phi}_r[\tilde{a}'(M_i,N_j)\Delta^2_{m,n}+n\tilde{b}'(M_i,N_j)\Delta^1_{m,n}]\,,$$

$$\vec{\tilde{\mathrm{f}}}_{SM_i,CN_j}=\hat{\phi}_r[\tilde{a}'(M_i,N_j)\Delta^2_{n,m}-n\tilde{b}'(M_i,N_j)\Delta^3_{m,n}], \tag{A7}$$

$$\tilde{g}_{CM_i,CN_j}=\tilde{g}_{SM_i,SN_j}=\left[\tilde{d}'(M_i,N_j)-\frac{1}{r_n}\tilde{e}'(M_i,N_j)-\frac{mn}{r_n}\tilde{f}'(M_i,N_j)\right]\bar{\delta}_{m,n}$$

$$+\frac{m\cot\theta_r}{r_n}\tilde{a}'(M_i,N_j)\Delta^2_{n,m}-\frac{mn\cot\theta_r}{r_n}\tilde{b}'(M_i,N_j)\Delta^3_{m,n}\,,$$

$$\tilde{g}_{CM_i,SN_j}=\tilde{g}_{SM_i,CN_j}=0\,,$$

where $\tilde{a}'(M_i, N_j) = \int M_i \left[\frac{\partial N_j}{\partial r_\mu} \sin\theta + \frac{\cos\theta}{r_\mu} \frac{\partial N_j}{\partial \theta}\right] \cos^2\phi\, d^3r_\mu$, $\tilde{b}'(M_i, N_j) = \int \frac{M_i N_j}{r_\mu \sin\theta} \cos^2\phi\, d^3r_\mu$,

$$\tilde{c}'(M_i, N_j) = \int M_i \left[\frac{\partial N_j}{\partial r_\mu} \cos\theta - \frac{\sin\theta}{r_\mu} \frac{\partial N_j}{\partial \theta}\right] \cos^2\phi\, d^3r_\mu \ ,$$

$$\tilde{d}'(M_i, N_j) = \int \frac{\partial M_i}{\partial r_n} \left[\frac{\partial N_j}{\partial r_\mu} \cos\theta - \frac{\sin\theta}{r_\mu} \frac{\partial N_j}{\partial \theta}\right] \cos^2\phi\, d^3r_\mu \ , \tag{A8}$$

$$\tilde{e}'(M_i, N_j) = \int \frac{\partial M_i}{\partial \theta} \left[\frac{\partial N_j}{\partial r_\mu} \sin\theta + \frac{\cos\theta}{r_\mu} \frac{\partial N_j}{\partial \theta}\right] \cos^2\phi\, d^3r_\mu \ , \quad \tilde{f}'(M_i, N_j) = \int [M_i N_j \cot\theta / r_\mu \sin\theta] \cos^2\phi\, d^3r_\mu \ .$$

As before, note that $\tilde{\tilde{\mathrm{f}}}_{CM_i, SN_j}$ and $\tilde{\tilde{\mathrm{f}}}_{SM_i, CN_j}$ have no ϕ_r dependence, and that we are dealing with $L_z = 0$ states only, therefore we have from (12b)

$$\tilde{\Theta}_{CM_i, SN_j} = \tilde{\Theta}_{SM_i, CN_j} = 0. \tag{A9}$$

Equations (24) follow from (A7)–(A9), where

$$\tilde{a}(M_i, N_j) = \tilde{a}'(M_i, N_j), \ldots, \tilde{f}(M_i, N_j) = \tilde{f}'(M_i, N_j), \quad \text{for } m \geq 1, \ n \geq 1 \ ;$$

$$\tilde{a}(M_i, N_j) = 2\tilde{a}'(M_i, N_j), \ldots, \tilde{f}(M_i, N_j) = 2\tilde{f}'(M_i, N_j), \quad \text{for } m \text{ and/or } n = 0 \ .$$

APPENDIX B

We transform the integrals $a, \ldots, f$ and $\tilde{a}, \ldots, \tilde{f}$ into spheroidal coordinates, which are the ones in which the two-fixed-center solutions are usually evaluated.

$$\text{Let} \quad r_n, r_\mu, \theta \to r_n, \lambda, \mu, \tag{B1}$$

$$\text{where} \quad \lambda = (r_{2\mu} + r_{1\mu})/r_n \ , \quad \mu = (r_{2\mu} - r_{1\mu})/r_n \ . \tag{B2}$$

$$\text{Then} \quad r_\mu^2 \sin\theta\, d\theta\, dr_\mu \to (r_n^3/8)(\lambda^2 - \mu^2) d\mu\, d\lambda, \quad 1 \leq \lambda \leq \infty, \quad -1 \leq \mu \leq 1 \ , \tag{B3}$$

and letting $\int \cos^2\phi\, d\phi = \pi$ in the integrals of Appendix A, we get

$$a'(M_i, N_j) = \frac{\pi r_n^3}{8} \int M_i \left\{ -\mu(\lambda^2 - 1)^{1/2}(1 - \mu^2)^{1/2} \frac{\partial N_j}{\partial \lambda} + \lambda(\lambda^2 - 1)^{1/2}(1 - \mu^2)^{1/2} \frac{\partial N_j}{\partial \mu} \right\} d\mu\, d\lambda \ ,$$

$$b'(M_i, N_j) = (\pi r_n^3/8) \int M_i N_j \{ -\lambda\mu(\lambda^2 - \mu^2)/(\lambda^2 - 1)^{1/2}(1 - \mu^2)^{1/2} \} d\mu\, d\lambda \ ,$$

$$c'(M_i, N_j) = \frac{\pi r_n^3}{8} \int M_i \left\{ (\lambda^2 - \mu^2) \frac{\partial N_j}{\partial r_n} - \frac{\lambda(\lambda^2 - 1)}{r_n} \frac{\partial N_j}{\partial \lambda} - \frac{\mu(1 - \mu^2)}{r_n} \frac{\partial N_j}{\partial \mu} \right\} d\mu\, d\lambda \ ,$$

$$d'(M_i, N_j) = \frac{\pi r_n^3}{8} \int \left\{ \frac{\partial M_i}{\partial r_n} - \frac{\lambda(\lambda^2 - 1)}{r_n(\lambda^2 - \mu^2)} \frac{\partial M_i}{\partial \lambda} - \frac{\mu(1 - \mu^2)}{r_n(\lambda^2 - \mu^2)} \frac{\partial M_i}{\partial \mu} \right\} \tag{B4}$$

$$\times \left\{ (\lambda^2 - \mu^2) \frac{\partial N_j}{\partial r_n} - \frac{\lambda(\lambda^2 - 1)}{r_n} \frac{\partial N_j}{\partial \lambda} - \frac{\mu(1 - \mu^2)}{r_n} \frac{\partial N_j}{\partial \mu} \right\} d\mu\, d\lambda \ ,$$

$$e'(M_i,N_j)=\frac{\pi r_n^{\,3}}{8}\int\left\{\frac{-\mu(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}}{(\lambda^2-\mu^2)}\frac{\partial M_i}{\partial\lambda}+\frac{\lambda(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}}{(\lambda^2-\mu^2)}\frac{\partial M_i}{\partial\mu}\right\}$$
$$\times\left\{-\mu(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\frac{\partial N_j}{\partial\lambda}+\lambda(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}\frac{\partial N_j}{\partial\mu}\right\}d\mu\,d\lambda\ ,$$

$$f'(M_i,N_j)=(\pi r_n^{\,3}/8)\int M_iN_j\{\lambda^2\mu^2(\lambda^2-\mu^2)/(\lambda^2-1)(1-\mu^2)\}\,d\mu\,d\lambda\ .$$

Similarly,

$$\tilde a'(M_i,N_j)=\frac{\pi r_n^{\,3}}{8}\int M_i\left\{\frac{2\lambda}{r_n}\frac{\partial N_j}{\partial\lambda}-\frac{2\mu}{r_n}\frac{\partial N_j}{\partial\mu}\right\}(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}d\mu\,d\lambda\ ,$$

$$\tilde b'(M_i,N_j)=(\pi r_n^{\,3}/8)\int[2M_iN_j(\lambda^2-\mu^2)/r_n(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}]d\mu\,d\lambda\ ,$$

$$\tilde c'(M_i,N_j)=\frac{\pi r_n^{\,3}}{8}\int M_i\left\{\frac{-2\mu(\lambda^2-1)}{r_n}\frac{\partial N_j}{\partial\lambda}-\frac{2\lambda(1-\mu^2)}{r_n}\frac{\partial N_j}{\partial\mu}\right\}d\mu\,d\lambda\ ,$$

$$\tilde d'(M_i,N_j)=\frac{\pi r_n^{\,3}}{8}\int\left\{\frac{\partial M_i}{\partial r_n}-\frac{\lambda(\lambda^2-1)}{r_n(\lambda^2-\mu^2)}\frac{\partial M_i}{\partial\lambda}-\frac{\mu(1-\mu^2)}{r_n(\lambda^2-\mu^2)}\frac{\partial M_i}{\partial\mu}\right\} \tag{B5}$$
$$\times\left\{\frac{-2\mu(\lambda^2-1)}{r_n}\frac{\partial N_j}{\partial\lambda}-\frac{2\lambda(1-\mu^2)}{r_n}\frac{\partial N_j}{\partial\mu}\right\}d\mu\,d\lambda\ ,$$

$$\tilde e'(M_i,N_j)=\frac{\pi r_n^{\,3}}{8}\int\left\{\frac{-\mu(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}}{(\lambda^2-\mu^2)}\frac{\partial M_i}{\partial\lambda}+\frac{\lambda(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}}{(\lambda^2-\mu^2)}\frac{\partial M_i}{\partial\mu}\right\}$$
$$\times\left\{\frac{2\lambda}{r_n}\frac{\partial N_j}{\partial\lambda}-\frac{2\mu}{r_n}\frac{\partial N_j}{\partial\mu}\right\}(\lambda^2-1)^{1/2}(1-\mu^2)^{1/2}d\mu\,d\lambda\ ,$$

$$\tilde f'(M_i,N_j)=(\pi r_n^{\,3}/8)\int M_iN_j\{-2\lambda\mu(\lambda^2-\mu^2)/r_n(\lambda^2-1)(1-\mu^2)\}d\mu\,d\lambda\ .$$

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student is presently evaluating the matrix element between states of different azimuthal quantum number, using the Hunter and Pritchard wave functions (see Ref. 11).

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[17]In general, for nonidentical nuclei, even in the adiabatic approximation one cannot choose such a simple form. Rather, a linear combination of odd and even P_μ components must be chosen (see Ref. 8).

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Hydrogenic- and Sturmian-Function Expansions in Three-Body Atomic Problems*

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Hydrogenic-function and Sturmian-function expansions are examined in both the Schrödinger and Faddeev formulations for three-body atomic problems. A detailed comparison of their convergence behavior is made. The difficulty of Sturmian-function expansion in accounting for the strong coupling between degenerate target states at excitation thresholds does not arise in the Faddeev formulation. The difficulty with the uncontrolled continuum contribution in the hydrogenic-function expansion, however, persists in both formulations. An estimation of the continuum contribution in the hydrogenic-function expansion is made for off-shell amplitudes which appear in the Faddeev formulation.

I. INTRODUCTION

It is well known that a three-body scattering function which has a specified symmetry and angular momentum but which is otherwise arbitrary can always be expanded in terms of a complete set of two-body eigenfunctions. This then leads to a set of coupled integrodifferential equations for the three-body system. Since for most physical scattering processes, one encounters the scattering to two subsystems, consisting (for the present three-body system) of an incident particle and a two-body target subsystem in a certain bound state, the complete set of eigenfunctions of the two-body target subsystem constitutes, therefore, a natural set for the expansion.[1]

For atomic systems (with Coulomb potentials), the two-body target functions are hydrogenic functions which form a complete set only after continuum states are included. It was, therefore, generally felt that such a hydrogenic-function (HF) expansion would converge slowly since it involves continuum states. To avoid the continuum states, an alternative expansion in terms of Sturmian functions which form a complete set of discrete states has been proposed by Rotenberg.[2] It was hoped that the Sturmian-function (SF) expansion, containing no continuum states, would converge faster.

Subsequent investigation[3–9] of these two expansions in the Schrödinger formulation have found that both of these two expansions have undesirable limitations. It has been observed that the SF expansion converges in a oscillatory manner and cannot account for the strong coupling of the l-degenerate target states at excitation thresholds. The HF expansion, on the other hand, has the convergence problem associated with the uncontrolled error from continuum states. In addition, the straightforward expansion methods have also difficulties in relation to the correlation problems[8] and polarization interactions.[9]

A more serious drawback of the expansion method in the Schrödinger formulation is perhaps in the treatment of rearrangement collisions. For such a problem, there is no unique set of states available for the formulation of the close-coupling equations suitable for both scattering and rearrangement channels. The powerful projection operator method formulated by Feshbach[10] provides very