Hyperspherical asymptotics of a system of four charged particles

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We present a detailed analysis of the charged four-body system in hyperspherical coordinates in the large hyperradial limit. In powers of \( R^{-1} \) for any masses and charges, the adiabatic Hamiltonian is expanded to third order in the dimer-dimer limit and to first order in the particle-trimer limit.

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I. INTRODUCTION

The Born-Oppenheimer approach for diatomic molecules leads to understandable one-dimensional potentials as a function of the internuclear distance. Generalizing to more degrees of freedom, the hyperspherical coordinates defines a collective adiabatic coordinate, the hyperradius \( R \), and treats all other degrees of freedom as “fast” coordinates [1, 2]. In this way, we keep our intuitive Born-Oppenheimer-like picture for ever larger systems, though the challenge remains in solving the resulting adiabatic Hamiltonian for each fixed value of \( R \).

Many few-body systems have been analyzed using the hyperspherical framework. For example, nuclear systems [3, 4] utilizing an expansion in hyperspherical harmonics [5, 6], systems of resonant short-range interactions [2, 7, 8], and systems of three charges [1, 10, 11] to name several. Hyperspherical methods have also been applied to molecular rearrangement collisions in physical chemistry, as discussed by Kuppermann for systems having up to five atoms in Ref. 20, and references therein. Charged systems in particular are interesting due to the long-range nature of the interactionsand because of their obvious relevance to many different physical processes in nature. Also of note are several treatments of the four-body Coulomb problem with one massive nucleus and three electrons, specifically [21, 22]. And there has even been some work addressing atoms with more than three electrons, e.g. the five-body system consisting of a nucleus surrounded by four electrons treated in Ref. 24.

The interplay between bound ionic complexes in the field of the remaining charges is complicated to describe on an equal footing. Moreover, the different types of fragmentation in molecules are usually treated entirely differently, with a separate class of methods for ionization channels of the \( \text{H}_2 \) molecule, for instance, than are utilized for molecular dissociation into neutrals or ions. This is one reason why a hyperspherical description could be fruitful, in that all fragmentation processes can then be mapped into a single coordinate \( R \) approaching infinity. The leading-order behavior in \( R \) also shows the dominant long-range potentials, e.g. van der Waals or ionic, that characterize such systems.

The present study generalizes the three-body asymptotic analysis of Macek [10], considering here the four-body system of charges in the asymptotic limit. We consider the dimer-dimer and particle-trimer asymptotic arrangements. In hyperspherical coordinates, the adiabatic Hamiltonian is expanded in powers of \( R^{-1} \), taking the dimer-dimer limit to third order and the particle-trimer limit to first order. Each term in the expansion is identified with analogous terms of a multipole expansion between charged clusters. The rest of the paper is organized as follows: Sec. II defines the Hamiltonian and the conversion to hyperspherical coordinates. Section III focuses on the dimer-dimer configuration while Sec. IV focuses on the particle-trimer configuration. Section V concludes.

II. THEORETICAL BACKGROUND

Consider the four-body system in three dimensions interacting via a sum of two-body Coulomb potentials. The Hamiltonian \( H \) in atomic units (\( \hbar = m_e = 1 \)) reads

\[
H = \sum_{j=1}^{4} \frac{-1}{2m_j} \nabla_j^2 + \sum_{i<j} \frac{q_i q_j}{|r_i - r_j|}
\]

where \( r_j, m_j, \) and \( q_j \) are the location, mass, and charge of particle \( j \). The center of mass \( H_{\text{CM}} \) and relative \( H_{\text{rel}} \) contributions separate, \( H = H_{\text{CM}} + H_{\text{rel}} \) and our interest centers on the relative Hamiltonian,

\[
H_{\text{rel}} = -\frac{1}{2\mu} \sum_{j=1}^{3} \nabla_j^2 \rho_j + V_C(\rho_1, \rho_2, \rho_3),
\]

where \( V_C \) contains the pair-wise Coulomb interactions as a function of the three relative Jacobi vectors \( \rho_j, j = 1, 2, 3 \). The Jacobi vectors are scaled such that they are analogous to three equal-mass “particles” of mass \( \mu \).

The hyperradial mass \( \mu \) is arbitrary, but for a unitary transformation

\[
\mu = \left( \frac{m_1 m_2 m_3 m_4}{m_1 + m_2 + m_3 + m_4} \right)^{1/3},
\]

which is assumed for the rest of this work. Under this transformation the volume element \( dV \) associated with the relative degrees of freedom is \( dV = d\rho_1 d\rho_2 d\rho_3 \).
The relative Hamiltonian $H_{rel}$ is recast in hyperspherical coordinates in terms of eight hyperangles denoted by $\Omega$ and a single length, the hyperradius $R$. The relative Hamiltonian is then a sum of the hyperradial kinetic energy $T_R$, the hyperangular kinetic energy $T_{\Omega}$, and the interaction potential,

$$H_{rel} = T_R + T_{\Omega} + V_{\text{int}}(R, \Omega).$$

(4)

Here,

$$T_R = -\frac{1}{2\mu} \frac{1}{R^8} \frac{\partial}{\partial R} R^8 \frac{\partial}{\partial R}$$

and

$$T_{\Omega} = \frac{\Lambda^2}{2\mu R^2},$$

(6)

where $\Lambda$ is the grand angular momentum operator. The exact form of the interaction potential $V_{\text{int}}$ and the square of the grand angular momentum operator depend on the choice of Jacobi vectors and the hyperangles. In Secs. III and IV we choose the H-type and K-type trees, respectively [8].

The Jacobi vectors $\rho_j$ are recast in terms of the hyperradius $R$ and the eight hyperangles $\alpha, \beta, \theta_1, \phi_1, \theta_2, \phi_2, \theta_3,$ and $\phi_3$. Here, $\theta_j$ and $\phi_j$ are defined as the usual polar and azimuthal angles of the Jacobi vector $\rho_j$ ($0 \leq \theta_j \leq \pi$ and $0 \leq \phi_j \leq 2\pi$) while the hyperangles $\alpha$ and $\beta$ are defined via

$$\tan \alpha = \frac{\rho_1}{\rho_2},$$

and

$$\tan \beta = \sqrt{\frac{\rho_1^2 + \rho_2^2}{\rho_3^2}}$$

(8)

where

$$\rho_1 = R \sin \alpha \sin \beta,$$

$$\rho_2 = R \cos \alpha \sin \beta,$$

$$\rho_3 = R \cos \beta,$$

(9)(10)(11)

and $R^2 = \rho_1^2 + \rho_2^2 + \rho_3^2$. The ranges of the hyperangles $\alpha$ and $\beta$ are restricted to $0 \leq \beta \leq \pi/2$ and $0 \leq \alpha \leq \pi/2$ because the $\rho_1$ are all positive. With these definitions, the square of the grand angular momentum operator is

$$\Lambda^2 = -\left( \frac{\partial^2}{\partial \beta^2} + \frac{5}{\tan \beta} - 2 \tan \beta \frac{\partial}{\partial \beta} \right)$$

$$+ \frac{1}{\sin^2 \beta} \left( \frac{\partial^2}{\partial \alpha^2} + \frac{4}{\tan(2\alpha)} \frac{\partial}{\partial \alpha} \right)$$

$$+ \frac{L_1^2}{\sin^2 \alpha \sin^2 \beta} + \frac{L_2^2}{\cos^2 \alpha \sin^2 \beta} + \frac{L_3^2}{\cos^2 \beta},$$

(12)

where

$$L_j^2 = -\left( \frac{\partial^2}{\partial \theta_j^2} + \cot \theta_j \frac{\partial}{\partial \theta_j} + \frac{1}{\sin^2 \theta_j} \frac{\partial^2}{\partial \phi_j^2} \right).$$

(13)

is the square of the angular momentum operator with eigenvalue $l_j(l_j+1)$ associated with the Jacobi vector $\rho_j$. The volume element is $dV = R^8 dR d\Omega$, where $d\Omega = \sin^2 \alpha \cos^2 \alpha \sin^5 \beta \cos^2 \beta d\theta d\phi d\rho_1 d\rho_2 d\rho_3$ and $d\rho_j = \sin \theta_j d\theta_j d\phi_j$.

The solution $\Psi_E(R, \Omega)$ to Eq. (4) is expanded in terms of the scaled radial $F_{E\nu}(R)$ and scaled channel functions $\Phi_{\nu}(R, \Omega)$,

$$\Psi_E(R, \Omega) = \sum \nu F_{E\nu}(R) \Phi_{\nu}(R, \Omega),$$

(14)

where

$$F_{E\nu}(R) = R^{-4} \tilde{F}_{E\nu}(R)$$

(15)

and

$$\Phi_{\nu}(R, \Omega) = (\sin \alpha \cos \alpha \sin^2 \beta \cos \beta)^{-1} \Phi_{\nu}(R, \Omega).$$

(16)

The channel functions at a fixed hyperradius $R$ form a complete orthonormal set over the hyperangles,

$$\int d\Omega \Phi^*_{\nu}(R, \Omega) \Phi_{\nu'}(R, \Omega) = \delta_{\nu\nu'},$$

(17)

and are the solutions to the adiabatic Hamiltonian $H_{ad}(R, \Omega)$,

$$H_{ad}(R, \Omega) \Phi_{\nu}(R, \Omega) = E_{\nu}(R) \Phi_{\nu}(R, \Omega),$$

(18)

where

$$H_{ad} = \frac{\Lambda^2}{2\mu R^2} + \frac{C(\Omega)}{R}$$

(19)

and $C(\Omega)$ is the hyperangular part of the Coulomb interaction. The scaled form of the square of the grand angular momentum operator $\bar{\Lambda}^2$ in the form that acts directly on $\Phi$ is

$$\bar{\Lambda}^2 = -\left( \frac{\partial^2}{\partial \beta^2} + \frac{1}{\tan \beta} \frac{\partial}{\partial \beta} + \frac{1}{\sin^2 \beta} \frac{\partial^2}{\partial \alpha^2} \right)$$

$$+ \frac{L_1^2}{\sin^2 \alpha \sin^2 \beta} + \frac{L_2^2}{\cos^2 \alpha \sin^2 \beta} + \frac{L_3^2}{\cos^2 \beta}.$$  

(20)

Note that a term $4/\sin^2 \beta$ from scaling in $\alpha$ cancels with a similar term from scaling in $\beta$. Also a term of 12 from scaling in $\beta$ cancels with a similar term from scaling in the hyperradius $R$. The scaled volume element $d\bar{V}$ is $d\bar{V} = dR d\bar{\Omega}$ where

$$d\bar{\Omega} = \sin \beta d\theta d\phi d\rho_1 d\rho_2 d\rho_3.$$  

(21)

After applying the relative Hamiltonian Eq. (4) on the expansion Eq. (14) and projecting from the left onto the complete set of channel functions, the Schrödinger equation reads

$$\left( -\frac{1}{2\mu} \frac{d^2}{dR^2} + U_{\nu}(R) - E \right) F_{E\nu}(R)$$

$$- \frac{1}{2\mu} \sum \nu' \left( 2P_{\nu\nu'}(R) \frac{d}{dR} + Q_{\nu\nu'}(R) \right) F_{E\nu'}(R) = 0.$$  

(22)
The hyperspherical Schrödinger equation Eq. (22) is solved in a two step procedure. First, \( H_{ad}(R, \Omega) \) is solved parametrically in \( R \) for the adiabatic potential curves \( U_\nu(R) \). In a second step, the coupled set of one-dimensional equations in \( R \) are solved. In Eq. (22), \( P_{\nu \nu'} \) and \( Q_{\nu \nu'} \) represent the coupling between channels, where

\[
P_{\nu \nu'}(R) = \left\langle \frac{\partial \bar{\Phi}_{\nu'}}{\partial R} \right\rangle \Omega
\]

and

\[
Q_{\nu \nu'}(R) = \left\langle \frac{\partial^2 \bar{\Phi}_{\nu'}}{\partial R^2} \right\rangle \Omega .
\]

The brackets indicate that the integrals are taken only over the hyperangles e.g. like in Eq. (17), with the hyperradius \( R \) held fixed.

### III. DIMER-DIMER CONFIGURATION

#### A. Coordinate system and Coulomb interaction

To describe the fragmentation into two dimers at large hyperradius \( R \), it is convenient to choose the H-type set of Jacobi vectors. The relative coordinates are defined via the coordinate transformation, conveniently written in matrix form, as

\[
\begin{pmatrix}
\rho_1 \\
\rho_2 \\
\rho_3 \\
R_{CM}
\end{pmatrix} = \begin{pmatrix}
\sqrt{\frac{\mu_{12}}{\mu}} \times \begin{bmatrix} 1 & -1 & 0 & 0 \end{bmatrix} \\
\sqrt{\frac{\mu_{34}}{\mu}} \times \begin{bmatrix} 0 & 0 & 1 & -1 \end{bmatrix} \\
\frac{1}{M_4} \times \begin{bmatrix} m_1 & m_2 & m_3 & m_4 \end{bmatrix}
\end{pmatrix} \begin{pmatrix}
\rho_1 \\
\rho_2 \\
\rho_3 \\
\rho_4
\end{pmatrix}
\]

where first \( \rho_1 \) is joined to \( \rho_2 \) (which defines \( \rho_1 \)) and \( \rho_3 \) is joined to \( \rho_4 \) (which defines \( \rho_2 \)), then the center of mass of each subcluster is joined to define \( \rho_3 \). The reduced masses are \( \mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \), \( \mu_{34} = \frac{m_3 m_4}{m_3 + m_4} \), and \( \mu_{dd} = (m_1 + m_2)(m_3 + m_4)/M_4 \). Also,

\[
M_N = m_1 + \cdots + m_N,
\]

that is, \( M_N \) is the total mass of the first \( N \) particles. The following considers only dimer-dimer channels of the type (12)+(34), but the same analysis can be similarly developed for the other fragmentation possibilities.

The Coulomb part \( V_C \) is straightforward to calculate in Jacobi coordinates, where the matrix from Eq. (23) is first inverted to define the \( \rho_j \) in terms of the \( \rho_i \). With the \( \rho_j \) defined, taking vector differences is straightforward.

\[
V_C = q_1 q_2 \sqrt{\frac{\mu_{12}/\mu}{\rho_1}} + q_1 q_3 \sqrt{\frac{\mu_{12}/\mu}{m_1}} \rho_1 - \sqrt{\frac{\mu_{34}/m_3}{m_1}} \rho_2 + \sqrt{\frac{\mu}{\mu_{dd}}} \rho_3 |^{-1} + q_1 q_4 \sqrt{\frac{\mu_{12}/m_1}{m_4}} \rho_1 + \sqrt{\frac{\mu_{34}/m_4}{m_1}} \rho_2 + \sqrt{\frac{\mu}{\mu_{dd}}} \rho_4 \]

\[
+ q_2 q_3 \sqrt{\frac{\mu_{12}/m_2}{m_3}} \rho_1 + \sqrt{\frac{\mu_{34}/m_3}{m_2}} \rho_2 - \sqrt{\frac{\mu}{\mu_{dd}}} \rho_3 |^{-1} + q_2 q_4 \sqrt{\frac{\mu_{12}/m_2}{m_4}} \rho_1 - \sqrt{\frac{\mu_{34}/m_4}{m_2}} \rho_2 - \sqrt{\frac{\mu}{\mu_{dd}}} \rho_3 |^{-1} + q_3 q_4 \sqrt{\frac{\mu_{34}/\mu}{\rho_2}} \]

(27)
Recasting the above expression in hyperspherical coordinates yields

\[
C(\Omega) = q_1q_2 \frac{\sqrt{\mu_{12}/\mu}}{\sin \alpha \sin \beta} + q_1q_3 \left[ \frac{\mu_{12}}{m_1^2} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{34}}{m_3^2} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{dd}} \cos^2 \beta - \frac{\mu_{12}\mu_{34}}{m_1m_3} \sin(2\alpha) \sin^2 \beta \cos \Omega + \frac{\sqrt{\mu_{12}/\mu}}{\sqrt{\mu_{dd}/m_1}} \sin \alpha \sin(2\beta) \cos \theta_{13} + \frac{\sqrt{\mu_{34}/\mu}}{\sqrt{\mu_{dd}/m_3}} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{1/2}
+ q_1q_4 \left[ \frac{\mu_{12}}{m_1^2} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{34}}{m_3^2} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{dd}} \cos^2 \beta - \frac{\mu_{12}\mu_{34}}{m_1m_3} \sin(2\alpha) \sin^2 \beta \cos \Omega + \frac{\sqrt{\mu_{12}/\mu}}{\sqrt{\mu_{dd}/m_1}} \sin \alpha \sin(2\beta) \cos \theta_{13} + \frac{\sqrt{\mu_{34}/\mu}}{\sqrt{\mu_{dd}/m_3}} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{1/2}
+ q_2q_3 \left[ \frac{\mu_{12}}{m_2^2} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{34}}{m_3^2} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{dd}} \cos^2 \beta - \frac{\mu_{12}\mu_{34}}{m_2m_3} \sin(2\alpha) \sin^2 \beta \cos \Omega + \frac{\sqrt{\mu_{12}/\mu}}{\sqrt{\mu_{dd}/m_2}} \sin \alpha \sin(2\beta) \cos \theta_{13} + \frac{\sqrt{\mu_{34}/\mu}}{\sqrt{\mu_{dd}/m_3}} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{1/2}
+ q_2q_4 \left[ \frac{\mu_{12}}{m_2^2} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{34}}{m_3^2} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{dd}} \cos^2 \beta - \frac{\mu_{12}\mu_{34}}{m_2m_3} \sin(2\alpha) \sin^2 \beta \cos \Omega + \frac{\sqrt{\mu_{12}/\mu}}{\sqrt{\mu_{dd}/m_2}} \sin \alpha \sin(2\beta) \cos \theta_{13} + \frac{\sqrt{\mu_{34}/\mu}}{\sqrt{\mu_{dd}/m_3}} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{1/2}
+ q_3q_4 \frac{\sqrt{\mu_{34}/\mu}}{\cos \alpha \sin \beta}
\]

where \( \cos \theta_{ij} \) is the cosine of the angle between Jacobi vectors \( \rho_i \) and \( \rho_j \) and the identity \( 2 \sin x \cos x = \sin(2x) \) is used to simplify the expression.

\[d\Omega = R^{-2} \left\{ 1 - \frac{s_1^2 + s_2^2}{6R^2} + O(R^{-4}) \right\} ds_1 ds_2 d\rho_1 d\rho_2 d\rho_3.
\]

Integrals over the hyperangles in this asymptotic analysis are allowed to go to \( \infty \) in \( s_1 \) and \( s_2 \), which introduces only exponentially small errors at large \( R \) for the dimer-dimer channels under present consideration.

B. Effective Hamiltonian

The simultaneous limits \( R \to \infty \) and \( \beta \to 0 \), such that \( R\beta = \rho \), describe the situation where the centers of mass of the (1,2) and (3,4) dimers are far apart. Said differently, to lowest order the Jacobi vector \( \rho_3 \) that connects the centers of mass of the (1,2) and (3,4) dimers scales proportionally to the hyperradius \( R \).

The asymptotic expansion of \( H_{\text{ad}} \) is accomplished by setting \( \beta = \rho/R \) in Eqs. (20) and (25) and taking the asymptotic Taylor series around \( R \to \infty \). Inverse powers of the hyperradius \( R \) then count the order of the expansion. This expansion defines the effective Hamiltonian \( H_{\text{eff}} \)

\[
H_{\text{eff}} \approx H_0 + H_1 + H_2 + H_3 + O(R^{-4}),
\]

where the subscripts indicate the corresponding powers of \( R^{-1} \). In the following, to simplify the expansion we use another coordinate transformation, \( s_1 = \rho \sin \alpha \) and \( s_2 = \rho \cos \alpha \). The scaled hyperangular volume element

becomes

\[
d\bar{\Omega} = R^{-2} \left\{ 1 - \frac{s_1^2 + s_2^2}{6R^2} + O(R^{-4}) \right\} ds_1 ds_2 d\rho_1 d\rho_2 d\rho_3.
\]

C. Evaluating \( H_0 \)

The first order \( H_0 \) in the effective Hamiltonian is \( R \)-independent,

\[
H_0 = h_1 + h_2,
\]

where

\[
h_j = -\frac{1}{2\mu} \frac{\partial^2}{\partial s_j^2} + \frac{1}{2\mu} \frac{L_j^2}{s_j^2} - \frac{Z_j}{s_j}
\]

is the scaled hydrogenic Hamiltonian with "charge" \( Z_j \);

\[
Z_1 = -q_1q_2 \sqrt{\mu_{12}/\mu}
\]

and

\[
Z_2 = -q_3q_4 \sqrt{\mu_{34}/\mu}.
\]
Note, the first derivatives are removed due to scaling of the channel functions, see e.g. Eq. (16) and the resulting scaled hyperangular kinetic energy Eq. (20). The first two terms of Eq. (32) come from the expansion of Eq. (20), while the last term comes from the expansion of Eq. (28). The (bound) dimers form if the constituent dimer charges are of opposite sign. Assuming the constituent dimer charges are point particles of opposite sign, the unsymmetrized solutions to $H_0$ are a product of the 1-D scaled radial Coulomb solutions $u_{n_l}$ and a set of coupled spherical harmonics. For $s_j, j = 1, 2$, the radial solution $u_{n_l}(x_j)$, normalized with respect to $ds_j$, is

$$u_{n_l}(x_j) = \sqrt{\frac{\mu Z_j (n - l - 1)!}{n^2 (n + l)!}} e^{\frac{-\mu Z_j}{2 n^2}} x_j^{l+1} L_{n_l-1}^{2l+1}(x_j),$$

where $x_j = 2 \mu Z_j s_j / n$. The quantum numbers range from $n = 1, 2, \ldots$ and $l = 0, \ldots, n - 1$. Equation (35) solves Eq. (32) with eigenvalues $-\mu Z_j^2 / (2n^2)$, such that the zeroth-order energies $E_0$ are

$$E_0 = -\frac{\mu Z_j^2}{2n^2} - \frac{\mu Z_j^2}{2n^2}. \tag{36}$$

The full unsymmetrized solution $\Phi_0(R; \Omega)$ at this order is the product of radial solutions and spherical harmonics coupled to a total angular momentum $L$ and projection $M$,

$$\Phi_0(R; \Omega) = \mathcal{N}(R) u_{n_{l_1}}(R \beta \sin \alpha) \times u_{n_{l_2}}(R \beta \cos \alpha) Y_{LM}^l(\hat{\rho}_1, \hat{\rho}_2, \hat{\rho}_3). \tag{37}$$

Here,

$$Y_{LM}^l(\hat{\rho}_1, \hat{\rho}_2, \hat{\rho}_3) = \sum_m \langle l_1 m_1; l_2 m_2 | l_3 m_3 \rangle Y_{11m_1}(\hat{\rho}_1) Y_{12m_2}(\hat{\rho}_2) Y_{13m_3}(\hat{\rho}_3). \tag{38}$$

where $l$ and $m$ represent the full set of $l$ and $m$ quantum numbers and $\langle ; | ; \rangle$ is a Clebsch-Gordan coefficient. At this order, $R^0$, the $l$ and $m$ are good quantum numbers, but at higher orders in $R$, e.g. $R^{-2}$ or higher, they do not, in general, remain good quantum numbers. The $R$-dependent normalization $\mathcal{N}(R)$ is straightforward to calculate by demanding that

$$\int d\Omega \Phi^*_0(R; \Omega) \Phi_0(R; \Omega) = 1 \tag{39}$$

whereby

$$\mathcal{N} = R \left\{ 1 + \frac{\langle n_{l_1} | s_1^2 | n_{l_1} \rangle + \langle n_{l_2} | s_2^2 | n_{l_2} \rangle}{12 R^2} + O(R^{-4}) \right\}. \tag{40}$$

The terms $\langle ; | ; \rangle$ indicate standard radial hydrogenic matrix elements $[20]$. Ignoring the $R$ prefactor of Eq. (40) that cancels with that of the volume element Eq. (30), the volume element leads to effective off-diagonal elements of $\langle H_0 \rangle$ of order $R^{-2}$ if evaluated in the basis $\Phi_0$. The normalization, on the other hand, ensures that the diagonal elements of $\langle H_0 \rangle$ have corrections of higher order, $R^{-4}$. If this nonzero overlap due to the volume element is viewed as a perturbation, then it contributes at second order in perturbation theory leading to coupling at order $R^{-4}$. These higher-order couplings are not treated in this work.

D. Evaluating $H_1$

The hyperradius $R$ first enters the asymptotic expansion Eq. (20) of $H_{ad}$ at first order,

$$H_1 = \frac{d_1}{R} \tag{41}$$

with charge-mass coefficient $d_1$,

$$d_1 = (q_1 + q_2) (q_3 + q_4) \sqrt{\mu_d / \mu}. \tag{42}$$

This order vanishes if either of the bound dimers are charge neutral, e.g. if $q_2 \to -q_1$ or $q_4 \to -q_3$, as this term represents coupling between ionic dimers treated as point particles. Nevertheless, the zeroth order wave functions $\Phi_0(R; \Omega)$ remain the correct wave functions and, treating $R$ as a parameter, the action of $H_1$ is to shift all energies by the same amount.

The diagonal elements of $\langle H_1 \rangle$ are of order $R^{-2}$ when evaluated in the basis $\Phi_0$. Taking into account the volume element Eq. (30) and the normalization Eq. (40), the off-diagonal matrix elements of $\langle H_1 \rangle$ are of order $R^{-3}$ (and corrections to the diagonal matrix elements of order $R^{-5}$). Similar to the effect in $\langle H_0 \rangle$, if viewed as a perturbation, these off-diagonal corrections contribute at second order in perturbation theory. At that order, there are couplings at order $R^{-6}$, but these higher-order couplings are not treated in this work.

E. Evaluating $H_2$

At second order in Eq. (20),

$$H_2 = H_2^A + H_2^C, \tag{43}$$

where

$$H_2^A = \frac{1}{6 \mu R^2} \left\{ L_1^2 \left( 1 + \frac{s_1^2}{s_1^2} \right) + L_2^2 \left( \frac{s_1^2}{s_2^2} + 1 \right) + 3 L_3^2 
- s_1^2 \frac{\partial^2}{\partial s_1^2} - s_2^2 \frac{\partial^2}{\partial s_2^2} + 2 s_1 \frac{\partial}{\partial s_1} + 2 s_2 \frac{\partial}{\partial s_2} + 2 s_1 \frac{\partial}{\partial s_1} s_2 \frac{\partial}{\partial s_2} \right\} \tag{44}$$
comes from the expansion of the hyperangular kinetic energy Eq. (24) and

$$H_2^C = \frac{1}{R^2} \left\{ GD - \frac{Z_1}{6} \left( s_1 + \frac{s_2^2}{s_1} \right) - \frac{Z_3}{6} \left( \frac{s_3^2}{s_2} + s_2 \right) \right\}$$  \hspace{1cm} (45)$$

comes from the expansion of the Coulomb potential Eq. (28). The terms contained within “GD,”

$$GD = d_2^{(1)} \cos \theta_{13} + d_2^{(2)} s_2 \cos \theta_{23}$$  \hspace{1cm} (46)$$

are the hyperradial analog of the first-order multipole expansion. These terms lead to Gailitis-Damburg corrections \cite{27}, where the charge-mass coefficients $d_2^{(1)}$ and $d_2^{(2)}$ are

$$d_2^{(1)} = (q_3 + q_4) \left( \frac{q_2}{m_2} - \frac{q_1}{m_1} \right) \mu_{dd} \sqrt{\mu_{12}/\mu}$$  \hspace{1cm} (47)$$

and

$$d_2^{(2)} = (q_1 + q_2) \left( \frac{q_3}{m_3} - \frac{q_4}{m_4} \right) \mu_{dd} \sqrt{\mu_{34}/\mu} .$$  \hspace{1cm} (48)$$

As can be seen in Eqs. (47) and (48), if a dimer is charge neutral, then the corresponding first-order multipole expansion term vanishes. But if opposite parity levels of a fragmenting dimer are degenerate, as is the case for all hydrogenic systems in excited states, the Gailitis-Damburg terms must be diagonalized using degenerate perturbation theory \cite{28}.

If evaluated in the basis $|\Phi_0\rangle$, \langle $H_2^C \rangle$ remains diagonal within a degenerate subspace. Said differently, ignoring any accidental degeneracies only states with the same $n_1$ and $n_2$ but different sets of $l$ quantum numbers can couple. However, only the multipole expansion terms of $H_2^C$ introduce coupling within a degenerate manifold and efficient methods exist to calculate such off-diagonal matrix elements \cite{29}. Focusing on the diagonal elements \langle $\Phi_0 | H_2 | \Phi_0 \rangle$, after standard hydrogenic integrals and much algebra yields

$$\langle \Phi_0 | H_2 | \Phi_0 \rangle = \frac{l_3(l_3 + 1)}{2\mu R^2} + \langle \Phi_0 | GD | \Phi_0 \rangle$$ 
$$+ \frac{1}{4 \mu R^2} \left\{ -1 - n_1^2 + l_1(l_1 + 1) - n_2^2 + l_2(l_2 + 1) \right\}$$  \hspace{1cm} (49)$$

Motivated by low energy scattering, if we assume one of the dimers is in its ground state, then the coupling angular integrations from the multipole expansion terms simplify. In this case, Eq. (49) reduces to either $|A_{23}|$ or $|A_{13}|$, where

$$|A_{23}| = \sum_{m_2 m_3} (l_2 m_2; l_3 m_3 | LM) Y_{00}(\hat{p}_1) Y_{l_2 m_2}(\hat{p}_2) Y_{l_3 m_3}(\hat{p}_3)$$  \hspace{1cm} (50)$$

and

$$|A_{13}| = \sum_{m_1 m_3} (l_1 m_1; l_3 m_3 | LM) Y_{00}(\hat{p}_1) Y_{00}(\hat{p}_2) Y_{l_3 m_3}(\hat{p}_3).$$  \hspace{1cm} (51)$$

At this order, the only nonzero couplings are

$$\langle A'_{k3} | P_l(\cos \theta_{k3}) | A_{k3} \rangle = c_k c_3 (-1)^l \left\{ \frac{l_3}{l_2} \frac{l_3}{l_k} \frac{L}{l_l} \right\},$$  \hspace{1cm} (52)$$

$$k = 1, 2$$, with $l = 1$ in the Legendre polynomial $P_l$. Here,

$$c_j = (-1)^j \sqrt{2l_j + 1} l_j 0 \right\} \cdot 10 |l_j 0\rangle  \hspace{1cm} (53)$$

and \{ \ldots \} is a Wigner six-J symbol.

F. Evaluating $H_3$

The third-order correction comes exclusively from expansion of the Coulomb potential, Eq. (28).

$$H_3 = \frac{1}{R^3} \left\{ \frac{d_1}{2} (s_1^2 + s_2^2) - \frac{d_2^{(1)}}{d_1} s_1 s_2 (\cos \theta_{12} - 3 \cos \theta_{13} \cos \theta_{23}) \right\} - \frac{d_2^{(2)}}{d_1} s_1^2 (1 - 3 \cos^2 \theta_{13}) - \frac{d_3^{(1)}}{2} s_2^2 (1 - 3 \cos^2 \theta_{23}) ,$$  \hspace{1cm} (54)$$

where the charge-mass coefficients $d_1$, $d_2^{(1)}$, and $d_2^{(2)}$ are given in Eqs. (12), (47), and (48), respectively, while $d_3^{(1)}$ and $d_3^{(2)}$ are

$$d_3^{(1)} = (q_3 + q_4) \left( \frac{q_1}{m_1} + \frac{q_2}{m_2} \right) \frac{\mu_{34}^3 \mu_{12}^3}{\mu_{ij}^{1/2}} \hspace{1cm} (55)$$

and

$$d_3^{(2)} = (q_1 + q_2) \left( \frac{q_3}{m_3} + \frac{q_4}{m_4} \right) \frac{\mu_{34}^3 \mu_{12}^3}{\mu_{ij}^{1/2}} .$$  \hspace{1cm} (56)$$

The first term of Eq. (54) is unique to the hyperradial expansion. It is not analogous to any term from the multipole expansion in Jacobi coordinates. It vanishes if either of the dimers are charge neutral, or if non-vanishing, leads to additional couplings between channels. The last two terms are the second-order multipole expansion terms. The multipole term in $\theta_{13}$, coming from the $(1, 2)$ dimer, vanishes if the far $(3, 4)$ dimer is charge neutral, while the multipole term in $\theta_{23}$, coming from the $(3, 4)$ dimer, vanishes if the far $(1, 2)$ dimer is charge neutral. The middle term of Eq. (54) does not vanish if the dimers are bound and represents two interacting dipoles.

For completeness, assuming one dimer is in the ground state, the angular coupling from the last two terms of
Eq. [54] are given by Eq. [52] with $l = 2$. The only nonzero angular coupling from the middle term is

$$\langle A'_{13} | \cos \theta_{12} - 3 \cos \theta_{13} \cos \theta_{23} | A_{23} \rangle = \delta_{l_1} \delta_{l_2} \left\{ \frac{4\pi}{3} \delta_{l_3} - \frac{(-1)^{l_3 + l_3'}}{2L + 1} \sqrt{2l_3 + 1} \langle l_3; 0; 10 | L0 \rangle \right\}$$

(57)

G. Lowest order nonadiabatic couplings

To lowest order, the nonadiabatic couplings Eqs. [23] and [24] can be calculated using the zeroth-order wave function Eq. [37], neglecting the higher-order corrections to the normalization and the volume element. The derivations with respect to the hyperradius $R$ do not affect the polar angles $\hat{\rho}_j$ of the Jacobi vectors and these integrations are trivial. After performing the integration over the polar angles, the $P$ matrix between dimer-dimer states is

$$P_{\nu \nu'} = \delta_{\nu \nu'} \int R u_{n_1} (R \beta \sin \alpha) u_{n_2} (R \beta \cos \alpha) \times \frac{\partial}{\partial R} R u_{n_1'} (R \beta \sin \alpha) u_{n_2'} (R \beta \cos \alpha) R \beta d\beta d\alpha$$

$$= \frac{\delta_{\nu \nu'}}{R} \left\{ \delta_{n_1 n_2'} (n_1 | s_1 \partial_1 | n_1') + \delta_{n_1 n_1'} (n_2 | s_2 \partial_2 | n_2') + \delta_{n_1 n_1'} \delta_{n_2 n_2'} \right\}.$$  \hspace{1cm} (58)

Here, $\partial_j$ represent derivatives with respect to $s_j$. This long range coupling only occurs between dimer-dimer states of the same internal angular momentum, but different principle excitations.

The $Q$ matrix is

$$Q_{\nu \nu'} = \frac{\delta_{\nu \nu'}}{R^2} \left\{ 2 \delta_{n_2 n_2'} (n_1 | s_1 \partial_1 | n_1') + 2 \delta_{n_1 n_1'} (n_2 | s_2 \partial_2 | n_2') + \delta_{n_1 n_2'} (n_1 | s_1 \partial_1 | n_1') + \delta_{n_1 n_1'} (n_2 | s_2 \partial_2 | n_2') + 2 (n_1 | s_1 \partial_1 | n_1') (n_2 | s_2 \partial_2 | n_2') \right\}.$$  \hspace{1cm} (59)

The diagonal elements are

$$Q_{\nu \nu} = \frac{1}{2\mu} \left\{ -1 - n_1^2 + l_1 (l_1 + 1) - n_2^2 + l_2 (l_2 + 1) \right\},$$  \hspace{1cm} (60)

which can be seen match with the terms in curly brackets from Eq. [49]. Thus, taking the adiabatic potentials with nonadiabatic diagonal correction, the only remaining terms are an angular momentum barrier due to the inter-dimer angular momentum $l_3$ and the first-order multipole corrections. One key result of the present analysis is analogous to what Maccek found in the three-body system [10], namely that the combination of $U_{\nu}(R) - \frac{1}{\mu} Q_{\nu \nu}(R)$ at long range has the expected coefficient of $1/2\mu R^2$, namely $l_3 (l_3 + 1)$ (or the eigenvalues of the Gailitis-Damburg corrections in cases where they contribute in first-order degenerate perturbation theory). This is reassuring because it means that the asymptotic centrifugal barrier has the same coefficient in hyperspherical coordinates as it has in conventional Jacobi coordinates.

H. Special cases

An important case of fragmenting bound dimers is the case where they are identical. That is, if the equally-charged particles are identical fermions, then $m_1 = m_3 = m_A$ and $q_1 = q_3 = q_A$, and $m_2 = m_4 = m_B$ and $q_2 = q_4 = q_B$. In this case the wave function must be antisymmetric with respect to the two “A” particles and the two “B” particles. The corresponding antisymmetrizing operator is $1 - P_{13} - P_{24} + P_{13} P_{24}$ acting on the basis $| \Phi_0 \rangle$. The results $P_{13} | \Phi_0 \rangle$ and $P_{24} | \Phi_0 \rangle$, however, are exponentially suppressed due to the spatial part of the wave function in the asymptotic limit. This can be seen since these permutations rotate $\rho_1$ and $\rho_2$ such that they pick up components along all Jacobi vectors. Thus, in the asymptotic limit, the arguments of the hydrogenic wave functions are proportional to the asymptotically large hyper-radius. To a good approximation then the antisymmetrization is accomplished by $(1 + P_{13} P_{24}) | \Phi_0 \rangle$, where the action of the last operator is to swap $\rho_1$ and $\rho_2$ and reverse the direction of $\rho_3$.

Because the dimers are identical, there are also additional degeneracies to consider. For example, in general $(| \Phi_0 \rangle H_2 P_{13} P_{24} | \Phi_0 \rangle \neq 0$ and degenerate perturbation theory is required. This is true even for charge-neutral dimers, though the multipole expansion terms and any coupling thereof would be eliminated. For charge-neutral identical dimers, there is an additional symmetry where the system is invariant under charge conjugation. The charge conjugation projection operator $\hat{C}$, which can be written here as $\hat{C} = (1 + P_{12} P_{34})$, reverses the direction of $\rho_1$ and $\rho_2$, but leaves $\rho_3$ unchanged. Thus, the antisymmetrized channel functions $(1 + P_{13} P_{24}) | \Phi_0 \rangle$ are already eigenstates of $\hat{C}$ with eigenvalues $(-1)^{l_1 + l_2}$.

The equal mass and charge case includes the positronium dimer system, which is studied in more detail in Ref. [30].

IV. PARTICLE-TRIMER CONFIGURATION

A. Coordinate system and Coulomb interaction

To describe the break up into a trimer and free particle, it is convenient to choose the K-type set of Jacobi vectors. The relative coordinates are defined via the coordinate
transformation, conveniently written in matrix form, as

\[
\begin{pmatrix}
\rho_1 \\
\rho_2 \\
\rho_3 \\
R_{CM}
\end{pmatrix} = 
\begin{pmatrix}
\frac{\sqrt{\mu_{12}}}{\mu} \times \{1 & -1 & 0 & 0\} & r_1 \\
\frac{\sqrt{\mu_{12}}}{\mu} \times \{\frac{m_2}{m_1} & \frac{m_2}{m_1} & 0 \} & r_2 \\
\frac{\sqrt{\mu_{12}}}{\mu} \times \{\frac{m_3}{M} & \frac{m_3}{M} & 0 \} & r_3 \\
\frac{1}{M} \times \{m_1 & m_2 & m_3 & m_4\} & r_4
\end{pmatrix}, \quad (61)
\]

where first \(r_1\) is joined to \(r_2\) (which defines \(\rho_1\)), then the center of mass of this pair is joined to \(r_3\) (which defines \(\rho_2\)), and last the center of mass of the trimer cluster is joined to \(r_4\) (which defines \(\rho_3\)). \(M_3\) and \(M_4\) are defined in Eq. (20) and the newly introduced reduced masses are the atom-dimer mass \(\mu_{pt}\), \(\mu_{pt} = \frac{M_3 m_4}{M_4}\), and \(\mu_{123} = \frac{M}{m_1 m_2 m_3}\). Note, though all equations in Sec. III still apply, the hyperangles of this configuration are different from the dimer-dimer configuration.

The Coulomb part \(V_C\) is straightforward to calculate in Jacobi coordinates, where the matrix from Eq. (61) is first inverted to define the \(r_j\) in terms of the \(\rho_j\).

Expressing Eq. (62) in hyperspherical coordinates yields

\[
C(\Omega) = q_1 q_2 \sqrt{\frac{\mu_{12}}{\mu}} \left[ q_1 q_3 \left[ \frac{\mu_{12}}{m_1} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{12}}{m_2} \cos^2 \alpha \sin^2 \beta + \frac{\mu_{12}}{m_3} \cos^2 \beta \sin^2 \alpha \sin^2 \beta \sin(2\alpha) \sin^2 \beta \cos \theta_{12} \right]^{-1/2} \right. \\
+ q_1 q_4 \left[ \frac{\mu_{12}}{m_1} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{12}}{M_2} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{pt}} \cos^2 \beta \sin^2 \alpha \sin^2 \beta \sin(2\alpha) \sin^2 \beta \cos \theta_{12} \right. \\
+ \frac{\sqrt{\mu_{12}}}{\sqrt{\mu_{123}} m_1} \sin \alpha \sin(2\beta) \cos \theta_{13} + \left. \frac{\mu_{123}}{\mu_{pt} M_2} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{-1/2} \\
+ q_2 q_3 \left[ \frac{\mu_{12}}{m_2} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{12}}{m_3} \cos^2 \alpha \sin^2 \beta - \frac{\mu_{12}}{m_2 \sqrt{\mu_{123}}} \sin(2\alpha) \sin^2 \beta \cos \theta_{12} \right]^{-1/2} \\
+ q_2 q_4 \left[ \frac{\mu_{12}}{m_2} \sin^2 \alpha \sin^2 \beta + \frac{\mu_{12}}{M_2} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{pt}} \cos^2 \beta - \frac{\mu_{123}}{m_2 M_2} \sin(2\alpha) \sin^2 \beta \cos \theta_{12} \right. \\
- \frac{\sqrt{\mu_{12}}}{\sqrt{\mu_{pt} m_1}} \sin \alpha \sin(2\beta) \cos \theta_{13} + \left. \frac{\mu_{123}}{\mu_{pt} M_2} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{-1/2} \\
+ q_3 q_4 \left[ \frac{\mu_{123}}{m_3} \cos^2 \alpha \sin^2 \beta + \frac{\mu}{\mu_{pt}} \cos^2 \beta - \frac{\mu_{123}}{\sqrt{\mu_{pt} m_3}} \cos \alpha \sin(2\beta) \cos \theta_{23} \right]^{-1/2}. \quad (63)
\]

\[\text{B. Effective Hamiltonian}\]

The simultaneous limits \(R \to \infty\) and \(\beta \to 0\), such that \(R \beta = \rho\), describe the situation where the centers of mass of the (1,2,3) trimer and the remaining particle 4 are far apart. The asymptotic expansion of \(H_{ad}\) around \(R \to \infty\), where the terms are grouped in powers of \(1/R\), defines the effective Hamiltonian \(H_{eff}\),

\[
H_{eff} \approx H_0 + H_1 + H_2 + \mathcal{O}(R^{-3}). \quad (64)
\]

As was done in Sec. III to simplify the expansion we use another coordinate transformation, \(s_1 = \rho \sin \alpha\) and \(s_2 = \rho \cos \alpha\) resulting in the \(\alpha\) scaled hyperangular volume element of the same form as Eq. (50).

The first order \(H_0\) in the effective Hamiltonian Eq. (64) is \(R\)-independent, where

\[
H_0 = -\frac{1}{2\mu} \frac{\partial^2}{\partial s_1^2} + \frac{1}{2 \mu} L_1^2 - \frac{1}{2 \mu} \frac{\partial^2}{\partial s_2^2} + \frac{1}{2 \mu} L_2^2 + \sum_{i<j} V_{ij}. \quad (65)
\]
The interaction terms are

$$V_{12} = q_1 q_2 \sqrt{\mu_{12}/\mu} s_1,$$  \hspace{1cm} (66)

$$V_{13} = q_1 q_3 \frac{m_1 \sqrt{\mu_{13}/\mu}}{\mu_3 s_1 + m_1 s_2},$$  \hspace{1cm} (67)

and

$$V_{23} = q_2 q_3 \frac{m_2 \sqrt{\mu_{13}/\mu}}{\mu_3 s_1 - m_2 s_2},$$  \hspace{1cm} (68)

where

$$\mu_3 = \left( \frac{m_1 m_2 m_3}{m_1 + m_2 + m_3} \right)^{1/2}. \hspace{1cm} (69)$$

Equation (65) is recognizable as the scaled relative Coulomb three-body Hamiltonian, which has no known analytical solution but has been previously solved numerically to high accuracy using a number of approaches (see e.g. Refs. [25, 31–33] and references therein). The zeroth-order energies can be found in the suggested references and elsewhere. The hyperradius \( R \) first enters the asymptotic expansion Eq. (64) at first order,

$$H_1 = \frac{1}{R} (q_1 + q_2 + q_3) q_4 \sqrt{\mu pt/\mu}. \hspace{1cm} (70)$$

This order vanishes if the trimer is charge neutral, as this correction represents the ionic potential between the trimer and free particle. Similar to the dimer-dimer case, the effect of \( H_1 \) is to shift all energies by the same amount.

At second order,

$$H_2 = H_2^A + H_2^B \hspace{1cm} (71)$$

where \( H_2^A \) is of the same form as Eq. (44) and comes from the expansion of the hyperrangular kinetic energy Eq. (20). \( H_2^B \)

$$H_2^B = \frac{1}{6R^2} (s_1^2 + s_2^2) (V_{12} + V_{13} + V_{23}) + d_2^A s_1 \cos \theta_{13} + d_2^B s_2 \cos \theta_{23}, \hspace{1cm} (72)$$

comes from expansion of the Coulomb terms of Eq. (63). The charge-mass coefficients \( d_2^A \) and \( d_2^B \) are

$$d_2^A = q_4 \left( \frac{q_2}{\sqrt{\mu pt}} - \frac{q_1}{\sqrt{\mu_{123}}} \right) \frac{\mu_{12}/\mu_{123}^{3/2}}{m_1 \mu/\mu_{12}^{1/2}} \hspace{1cm} (73)$$

and

$$d_2^B = q_4 \left( \frac{q_3}{m_3} - \frac{q_1 + q_2}{M_2} \right) \frac{\mu_{12}^{1/2} \mu pt}{\mu^{1/2}}. \hspace{1cm} (74)$$

The last two terms of Eq. (72) are analogous to the first order terms of a multipole expansion of a charge distribution (the trimer) with a free charge. Our expectation is that the sum of the large-\( R \) adiabatic potential curve \( U_\nu(R) \) and the \( \frac{1}{\mu pt} Q_{\nu\nu}(R) \) terms cancel the first terms of Eq. (72) and all but the angular momentum barrier in \( l_3 \) of \( H_2^A \).

V. CONCLUSION AND OUTLOOK

This paper derives the asymptotic Hamiltonian in powers of \( R^{-1} \) for four-body systems of charges for both the dimer-dimer and particle-trimer dissociation configurations. The terms in the effective Hamiltonian are identified with analogous terms in the multipole expansion, with some complications associated with nonadiabatic couplings in the hyperrpherical representation. For the dimer-dimer configuration, diagonal matrix elements through order \( R^{-2} \) were calculated and off-diagonal couplings were discussed at this same order and higher. For the particle-trimer configuration, only up through second-order corrections in the effective Hamiltonian are derived.

The charged four-body system with arbitrary masses constitutes a large parameter space. In the adiabatic hyperrpherical framework, this work lends to the understanding of the dissociation of many systems such as \( \text{H}_2 \), \( \text{Ps}_2 \), three-electron atoms or other exotic muonic four-body clusters. Having analytical knowledge of the long-range tail of the potential curves also provides a check on numerical calculations of the adiabatic potentials and their nonadiabatic corrections.

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