Hyperspherical Elliptic Coordinates and Three-Body Coulomb Problem

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(Received 27 September 1994; revised manuscript received 16 December 1994)

We introduce the hyperspherical elliptic coordinates for the study of a class of three-body systems. These new coordinates are well adapted to the singularities of the three-body potential and may be regarded as a generalization of the familiar spheroidal coordinates for diatomic molecules. However, being defined on the hypersphere in six-dimensional space, the new coordinates formally resolve the long-standing difficulties of the Born-Oppenheimer ansatz such as the laborious evaluation of nonadiabatic coupling terms, a separate treatment of the mass-polarization effect, the need for the electronic translational factor, etc.

PACS numbers: 31.15.+Ta, 03.65.Nk, 34.10.+x

Recent experimental progress stimulated by the muon-catalyzed fusion project on the one hand and by hopes to get a closer insight on matter-antimatter coexistence on the other, has rendered exotic three-body Coulomb systems accessible. Among them Ps^- [1], $\bar{e}$-H [2], muonic molecules [3], mesic [4] and antiprotonic [5] helium, have complemented more routinely known two-electron atoms H^-, He, ... and diatomic molecular ions H_2^+, HeH^{2+}, ... giving a fresh incentive to theorists. From a theoretical viewpoint, the two mass ratios defined by the two attractive pairs provide key parameters of the problem. For real systems these parameters vary over more than 6 orders of magnitude. Whether the system as a whole forms a bound state or not is immaterial here. Indeed, experiment often centers on the observation of long-lived resonances and their decay. What is required of a satisfactory theory is the ability to handle the diverse mass ratios, to meet the need for treating excited resonant states, and to achieve the demanding high precision. This not only makes the subject challenging but exacerbates the difficulties.

Though the general case is forbidding, two imaginary systems $^\infty H^-$ and $^\infty H_2^+$, corresponding to two extreme limits of the mass ratios, permit a simplification. The former allows a single-center expansion on account of the infinite mass of the nucleus and the repulsive nature of the interelectronic interaction. The latter is a two-center problem; it is completely separable in spheroidal coordinates, providing the basis for many kinds of atomic calculations. These two limits play a fundamental role in our understanding of the three-body problem. It is vital that in either case there is a choice of coordinates whose singularities coincide with those of the attractive part of the three-body potential. The bound states confined in the potential wells can then be effectively expanded in products of one-dimensional functions. Here we present a new coordinate system whose singularities coincide with two singularities of the interparticle interaction for a general three-body system. In the two extreme limits, these coordinates transform to that of $^\infty H^-$ and $^\infty H_2^+$, though they are not of any known type when the masses are arbitrary.

Another facet of the three-body Coulomb problem that motivates the present work is the earlier application of the standard spheroidal coordinates to the solution of H^- and its isoelectronics [6]. Such an approach obviously amounts to regarding H^- and H_2^+ as twins, and leads to a rule of thumb that relates the energy level patterns between partners, hence to the level classification of H^- according to the quantum numbers of the diatomics. A major problem there is the inclusion of the strong nonadiabatic coupling due to the kinetic energy operator as well as the reordering of the zeroth order levels as a result of this inclusion. Though appealing, this approach therefore seems to miss an important physical element which turns out *a posteriori* to be the proper choice of the coordinate system addressed in this Letter.

The kinetic energy operator for the three-body system in a set of hyperspherical coordinates reads

$$T = -\frac{1}{2}(\Delta_{\mathbf{x}} + \Delta_{\mathbf{y}}) = -\frac{1}{2}\left(\frac{1}{R^5}\frac{\partial}{\partial R}R^5\frac{\partial}{\partial R} - \frac{\Lambda^2}{R^2}\right), \quad (1)$$

where $\mathbf{x}$ and $\mathbf{y}$ are the mass-scaled Jacobi vectors referred to the center-of-mass frame. For the sake of simplicity, we restrict ourselves here to the case of zero total angular momentum $L = 0$. The square of the grand angular momentum operator Λ^2 is then given by

$$\Lambda^2 = -\frac{4}{\sin^2\chi}\left\{\frac{\partial}{\partial\chi}\sin^2\chi\frac{\partial}{\partial\chi} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right\}. \quad (2)$$

The hyperradius R and two angular variables χ and θ are related to the Jacobi vectors as

$$R = \sqrt{\mathbf{x}^2 + \mathbf{y}^2}, \qquad \tan(\chi/2) = \frac{|\mathbf{y}|}{|\mathbf{x}|}, \qquad \cos\theta = \frac{(\mathbf{xy})}{|\mathbf{x}||\mathbf{y}|}, \quad (3a)$$

$$0 \le R \le \infty, \qquad 0 \le \chi \le \pi, \qquad 0 \le \theta \le \pi. \quad (3b)$$

The two-dimensional manifold S, spanned by χ and θ, together with the three Euler angles defining the

0031-9007/95/74(18)/3573(4)$06.00

orientation of the three-body triangle, form a hypersphere in the six-dimensional configurational space of the system. The potential energy V depends on three variables R, χ, and θ only, so only these three are relevant to the internal degrees of freedom. The restriction $L = 0$ imposed above permits one to disregard the Euler angles for now.

In the hyperspherical approach the relative motion of particles on the hypersphere of a fixed radius R and the radial breathing-type motion of the whole system are considered separately. One first has to solve the eigenvalue problem, parametrically dependent on R, for the adiabatic Hamiltonian $H_{\rm ad}$,

$$H_{\rm ad}\Phi = U(R)\Phi, \qquad H_{\rm ad} \equiv \tfrac{1}{2}\Lambda^2 + RC, \tag{4}$$

where $C \equiv RV$ is the effective charge, and then to include the effects of nonadiabaticity via standard close-coupling procedure. For Coulomb systems this approach was introduced by Macek, though it had a conceptual precursor in the Born-Oppenheimer expansion. Since the pioneering paper [7] the efficiency of this approach for $^{\infty}H^{-}$-like systems has been demonstrated by many authors (see [8], and references therein); the method works equally well for a wide range of energy spectra below the double ionization threshold, giving accuracy comparable to variational calculations [9]. For systems closer to the $^{\infty}H_2^{+}$ limit, such as muonic molecules, the nonadiabatic coupling is expected to be even smaller according to the Born-Oppenheimer argumentation. However, the difficulties in solving the adiabatic eigenvalue problem (4), caused by a sharp concentration of the wave function Φ near the two attractive Coulomb singularities of the effective charge C, prevented achieving an accuracy and efficiency comparable with the case of $^{\infty}H^{-}$. The actual reason for this lies in the inadequacy of the used coordinate system.

What is desirable to achieve by a proper choice of coordinates on S is to make some essential part of the three-body potential separable simultaneously with Λ^2. For the special case of $^{\infty}H^{-}$-like systems, the (χ, θ) coordinates satisfy these demands excellently; both attractive interactions admit separation simultneously with Λ^2, which actually underlies the efficiency of the numerical scheme used in [9]. However, for arbitrary masses these coordinates can be adapted only to one of the three interparticle interactions. There are two other known coordinate systems considered by Smith and Whitten [10] and by Simonov and Badalyan [11]. In both cases the operator Λ^2 is separable but, in spite of many nice properties, neither of them helps to diagonalize the adiabatic Hamiltonian.

We introduce new coordinates on S, which are somewhat resembling the elliptic coordinates in a plane. In order to illustrate the following construction it is convenient to represent S by one-half of a sphere in three-dimensional space ["eastern hemisphere," see (3b)] though it actually belongs to a hypersphere in six-dimensional space [12]. Here χ and θ correspond to the usual spherical angles θ and φ, respectively. Let Z be the axis from which the angle χ is measured (see Fig. 1). Consider the rotation of a set of Jacobi coordinates $(\mathbf{x}, \mathbf{y})$ into another set in six-dimensional space,

$$\begin{pmatrix} \mathbf{x}' \\ \mathbf{y}' \end{pmatrix} = \begin{pmatrix} -\cos\gamma & -\sin\gamma \\ \sin\gamma & -\cos\gamma \end{pmatrix} \begin{pmatrix} \mathbf{x} \\ \mathbf{y} \end{pmatrix}, \tag{5}$$

where γ may be regarded as an arbitrary parameter at this stage. This 6D rotation induces a rotation on the 3D image of S around its axis of symmetry by angle 2γ. Let Z' be the new position of the Z axis under this rotation. Using the new set $(\mathbf{x}', \mathbf{y}')$, similarly to (3a) primed variables $R' = R$, χ', and θ' can be defined, where the angle χ' is measured from the Z' axis. First, we transform (2) from (χ, θ) to another pair of independent variables (χ, χ'). The operator Λ^2 then acquires an explicitly symmetric form. Recognizing that χ and χ' play the role of a pair of "radial" variables on the sphere, measuring the "radial" distances from the Z and Z' axes, we define new coordinates in analogy to the construction of the spheroidal coordinates, namely,

$$\xi \equiv \chi + \chi', \qquad \eta \equiv \chi - \chi', \tag{6a}$$

$$2\gamma \le \xi \le 2\pi - 2\gamma, \qquad -2\gamma \le \eta \le 2\gamma. \tag{6b}$$

After some algebra, we come to our key equation,

$$\Lambda^2 = \frac{16}{\cos\eta - \cos\xi}\left\{\frac{\partial}{\partial\eta}(\cos 2\gamma - \cos\eta)\frac{\partial}{\partial\eta} - \frac{\partial}{\partial\xi}(\cos 2\gamma - \cos\xi)\frac{\partial}{\partial\xi}\right\}. \tag{7}$$

Thus, in the (ξ, η) coordinates the operator Λ^2 is clearly separable. These coordinates are illustrated in Fig. 1 [13]. The Z and Z' axes intersect the spherical shell

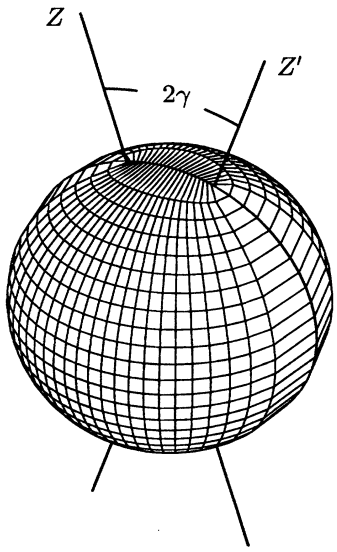

FIG. 1. Hyperspherical elliptic coordinates placed on the surface of a sphere in three-dimensional space ($\gamma = 0.3$). S manifold mentioned in the text corresponds to the front half of this sphere.

at four points $\{\xi = \pi \pm (\pi - 2\gamma), \eta = \pm 2\gamma\}$, which correspond to the singular points of the (ξ, η) coordinate system. The positions of these singularities depend on the rotation parameter γ. In the two degenerate limits $\gamma \to 0$ and $\gamma \to \pi/2$, two of the four singular points merge with two others, and formula (7) can be transformed back to (2). However, if one focuses on the behavior of the wave function only in the vicinity of the two merging foci, say $\{\xi = 2\gamma, \eta = \pm 2\gamma\}$ for $\gamma \to 0$ (this is the case of $^{\infty}H_2^+$), then curvature of S does not reveal itself, and by rescaling $\xi = 2\gamma\xi'$ and $\eta = 2\gamma\eta'$ the operator (7) reduces to the Laplace operator in the prolate spheroidal coordinates.

The general form of the effective charge in Eq. (4), which admits separation of variables simultaneously with Λ^2, reads

$$C_s(\xi, \eta) = \frac{a(\xi) + b(\eta)}{\cos\eta - \cos\xi}, \tag{8}$$

where $a(\xi)$ and $b(\eta)$ are arbitrary functions. For further purposes, it is convenient to define an auxiliary separable problem

$$H_{\rm ad}^{(s)}\Phi^{(s)} = U^{(s)}(R)\Phi^{(s)}, \qquad H_{\rm ad}^{(s)} \equiv \tfrac{1}{2}\Lambda^2 + RC_s. \tag{9}$$

Substituting the solution in the form $\Phi^{(s)} = f(\xi)g(\eta)$ leads to ordinary differential equations for $f(\xi)$ and $g(\eta)$

$$\left[8\frac{d}{d\xi}(\cos\xi - \cos 2\gamma)\frac{d}{d\xi} + Ra(\xi) + U^{(s)}(R)\cos\xi + A(R)\right]f(\xi) = 0, \tag{10a}$$

$$\left[8\frac{d}{d\eta}(\cos 2\gamma - \cos\eta)\frac{d}{d\eta} + Rb(\eta) - U^{(s)}(R)\cos\eta - A(R)\right]g(\eta) = 0, \tag{10b}$$

where $A(R)$ is a separation constant. These equations are similar to those encountered in the two-center Coulomb problem [14]. Equations (10) should be solved simultaneously subject to the regularity condition of $f(\xi)$ and $g(\eta)$ at the end points of the intervals (6b). This eigenvalue problem defines an infinite number of discrete pairs of eigenvalues $[U^{(s)}(R), A(R)]$; corresponding eigenfunctions $\Phi^{(s)}$ can be labeled by two indices n_1 and n_2, giving the numbers of zeros of $f(\xi)$ and $g(\eta)$. The system of $\Phi_{n_1n_2}^{(s)}$ provides a complete and orthogonal basis on S, which can be normalized with the volume element $dS = \pi^2(\cos\eta - \cos\xi)/4\sin 2\gamma\, d\xi\, d\eta$.

Now we turn to the three-body Coulomb system. Let m_i and Z_i $(i = 1, 2, 3)$ be the masses and charges of the particles. For definiteness, we assume that Z_1 and Z_2 are of the same sign, different from that of Z_3. To define the hyperspherical elliptic coordinates ξ and η, we introduce two sets of Jacobi vectors $(\mathbf{x}, \mathbf{y})$ and $(\mathbf{x}', \mathbf{y}')$, where $\mathbf{y}$ and $\mathbf{y}'$ join the pairs of oppositely charged particles 1-3 and 2-3, respectively. Then the rotation parameter γ in Eq. (5) is given by

$$\gamma = \arctan\sqrt{\frac{m_3(m_1 + m_2 + m_3)}{m_1m_2}}, \qquad 0 \le \gamma \le \pi/2. \tag{11}$$

The effective charge C as a function of ξ and η has the form

$$C(\xi, \eta) = 4\frac{\cos(\xi/2) + \cos(\eta/2)}{\cos\eta - \cos\xi} \times [q^+\sin(\xi/4)\cos(\eta/4) + q^-\cos(\xi/4)\sin(\eta/4)] + C_3, \tag{12}$$

where

$$q^{\pm} = Z_1Z_3\sqrt{\frac{m_1m_3}{m_1 + m_3}} \pm Z_2Z_3\sqrt{\frac{m_2m_3}{m_2 + m_3}}.$$

The first term in (12) includes both attractive interactions and has singularities at the two points $\{\xi = 2\gamma, \eta = \pm 2\gamma\}$, which coincide with two of four singular points of the (ξ, η) coordinate system. C_3 corresponds to the repulsion between particles 1 and 2; it has a singularity somewhere on the line $\xi = 2\pi - 2\gamma$, though its particular form is immaterial here. The two limiting cases of $^{\infty}H_2^+$ and $^{\infty}H^-$ correspond to $\gamma \to 0$ and $(\pi/2 - \gamma) \to 0$, respectively. The surface plots of the function $(\cos\eta - \cos\xi)C(\xi, \eta)$ for H_2^+ and H^- with real masses are shown in Fig. 2.

Formula (12) suggests splitting of $C(\xi, \eta)$ into two parts $C = C_s + C_r$, where C_s is of the form (8), thus it is separable, while the residue C_r can be diagonalized in the basis $\Phi_{n_1n_2}^{(s)}$ resulting from the solution of the separable part. This splitting is not unique, though for each particular system the appropriate choice of C_s, which minimizes the effect of C_r can be found. For H_2^+ and H^-, due to the smallness of γ or $(\pi/2 - \gamma)$, the functions shown in Fig. 2 exhibit only weak dependence on η or ξ, respectively. This gives a hint as to how to choose C_s in these two cases. The numerical procedure needed for solving the separable problem (10) and constructing a basis $\Phi_{n_1n_2}^{(s)}$ is similar to what is well developed in the two-center Coulomb problem [14]. The calculation of the matrix elements of C_r then can be done very effectively using the direct product of two one-dimensional quadratures, arising from the solution of (10). To test this algorithm we have calculated the ground state energy of H^-. Our result obtained with 45 coupled channels is $-0.527\,447$ which compares favorably with the best available variational calculation $-0.527\,445\,8811$ [15]. Note that with an increase of the number of channels the calculated result approaches its final value from below, and even 45 channels were found not enough to get convergence in the sixth digit. Additional inaccuracy of the order 10^{-6} may arise from the solution of close-coupled equations, though the accuracy of our adiabatic potential curves is estimated to be much better. The same method applied to H_2^+ gives for the ground state energy $-0.597\,144$. In

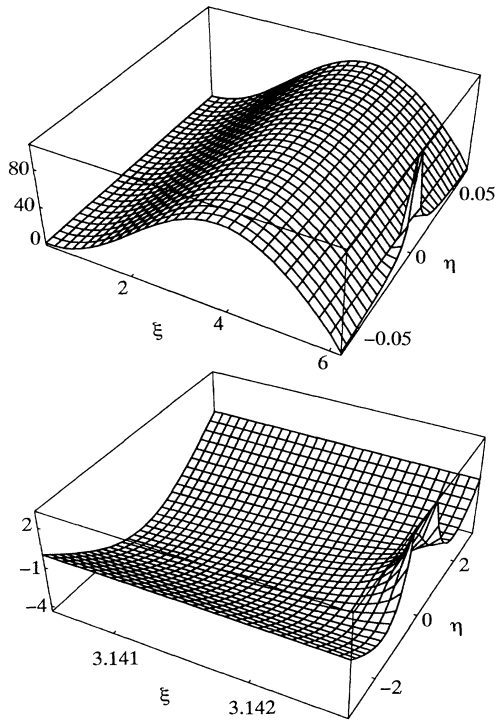

FIG. 2. Surface plots of the effective charge $C(\xi, \eta)$ times $(\cos\eta - \cos\xi)$ in hyperspherical elliptic coordinates: (a) H_2^+, $\gamma \approx 3.3 \times 10^{-2}$; (b) H^-, $(\pi/2 - \gamma) \approx 5.4 \times 10^{-4}$. The position of the repulsive singularity corresponds to $\eta = 0$, $\xi = 2(\pi - \gamma)$.

this case 36 channels ensure convergence within six digits, though even the one channel approximation gives a very small error, $\sim 10^{-4}$, as could be anticipated intuitively. We don't know any variational calculations of the ground state energy of H_2^+. The best known result $-0.597\,138$, obtained in the Born-Oppenheimer approximation with adiabatic correction [16], is a little higher than our converged value. The difference may arise from the inaccuracy of our close-coupled scheme, though it may be due to some imperfection of the adiabatic result [16] as well. We expect this method to apply to high-lying resonances with the same level of precision.

Without delving into details, we note the presence of the additional symmetry of the adiabatic Hamiltonian (4): For the special case of $\gamma = 0$, as well as for the general system in two limits $R = 0$ and $R \to \infty$, this symmetry is exact, giving an additional integral of motion $A(R)$. Otherwise the symmetry is broken by presence of C_r, though it still holds approximately, and this approximation is the better the sharper are regions of avoided crossing of adiabatic potential curves.

In conclusion, it seems quite possible that the hyperspherical approach armed by the hyperspherical elliptic coordinates is able to give, probably for the first time, a numerically consistent way of treating a wide spectrum of correlation and mass-polarization effects in the three-body Coulomb problem. We also believe that the coordinates introduced in this Letter could find their wide applications in theoretical study on chemical reactions [17].

We thank Dr. P. O'Mahony and Dr. H. Marxer for reading the manuscript and for giving useful comments. This work is partly supported by the Grant-in-Aid for Scientific Research on Priority Areas "Theory of Chemical Reactions—Computational Approach" from the Ministry of Education, Science, and Culture of Japan.

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[1] A. P. Mills, Jr., Phys. Rev. Lett. **46**, 717 (1981); **50**, 671 (1983).
[2] W. Sperber *et al.,* Phys. Rev. Lett. **68**, 3690 (1992); S. Zhou *et al., ibid.* **72**, 1443 (1994).
[3] W. H. Breunlich, P. Kammel, J. S. Cohen, and M. Leon, Annu. Rev. Nucl. Part. Sci. **39**, 311 (1989).
[4] T. Yamazaki *et al.,* Phys. Rev. Lett. **63**, 1590 (1989).
[5] M. Iwasaki *et al.,* Phys. Rev. Lett. **67**, 1246 (1991); N. Morita *et al., ibid.* **72**, 1180 (1994).
[6] J. M. Feagin and J. S. Briggs, Phys. Rev. A **37**, 4599 (1988); J. M. Rost and J. S. Briggs, J. Phys. B **22**, 3587 (1989).
[7] J. Macek, J. Phys. B **2**, 831 (1968).
[8] C. D. Lin, Adv. At. Mol. Phys. **22**, 77 (1986).
[9] J.-Z. Tang, S. Watanabe, and M. Matsuzawa, Phys. Rev. A **46**, 2437 (1992); J.-Z. Tang, Y. Wakabayashi, M. Matsuzawa, S. Watanabe, and I. Shimamura, *ibid.* **49**, 1021 (1994).
[10] F. T. Smith, J. Math. Phys. **3**, 735 (1962); R. C. Whitten and F. T. Smith, *ibid.* **9**, 1103 (1968).
[11] Yu. A. Simonov, Yad. Fiz. **3**, 630 (1966) [Sov. J. Nucl. Phys. **3**, 461 (1966)]; A. M. Badalyan and Yu. A. Simonov, *ibid.* **3**, 1032 (1966) [Sov. J. Nucl. Phys. **3**, 137 (1966)].
[12] A. Kuppermann, Chem. Phys. Lett. **32**, 374 (1975).
[13] The illustrative 3D visualization of S is based on a mapping procedure [14] whose foundation is deeper than it appears. There is a nontrivial correspondence between the operator (2) and the angular part of the 3D Laplacian. Indeed, separable coordinates on S induce separable coordinates on the 3D sphere, and vice versa. Hyperspherical elliptic coordinates R, ξ, and η embedded into three-dimensional space can be related to the conical coordinates, which is listed as case VI of the separable coordinate systems in P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Chap. 5.
[14] I. V. Komarov, L. I. Ponomarev, and S. Yu. Slavyanov, *Spheroidal and Coulomb Spheroidal Functions* (Nauka, Moscow, 1976).
[15] A. M. Frolov, J. Phys. B **26**, L845 (1993).
[16] C. L. Beckel, B. D. Hansen III, and J. Peek, J. Chem. Phys. **53**, 3681 (1970); G. Hunter, A. W. Yau, and H. O. Pritchard, At. Data Nucl. Data Tables **14**, 11 (1974).
[17] Y.-S. Mark Wu, A. Kuppermann, and B. Lepetit, Chem. Phys. Lett. **186**, 319 (1991); K. Nobusada, K. Sakimoto, and K. Onda, *ibid.* **216**, 613 (1993).