

# The potential energy surface of triplet $H_3^+$ : A representation in hyperspherical coordinates

P. E. S. Wormer and F. de Groot

*Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands*

(Received 9 March 1988; accepted 26 October 1988)

A large number of full CI calculations has been performed in order to obtain an accurate representation of the potential energy surface of the molecular ion  $H_3^+$  in its lowest triplet state. It is found that the surface is very flat, so that the molecule is very floppy and has a great likelihood of tunneling between the three symmetry-related minima. The potential is expanded in terms of elements of Wigner  $D$  matrices depending on hyperspherical angles. An extensive discussion of the Smith-Whitten hyperspherical coordinates, used in this work, is given.

## I. INTRODUCTION

The molecular ion  $H_3^+$  in its lowest singlet state has been known to exist since the beginning of this century. It is a rather rigid molecule with the shape of an equilateral triangle. Since Oka measured one of its vibrational bands in 1980,<sup>1</sup> interest in the molecule has been lively, not in the least because of its astrophysical importance. See, e.g., a paper by Meyer, Botschwina, and Burton<sup>2</sup> for a review on the experimental and theoretical work on this ion. These authors have performed an extensive set of *ab initio* calculations on the potential energy surface (PES) and the rovibrational spectrum of  $H_3^+$ . Tennyson and Sutcliffe<sup>3</sup> used recently the older potential of Schinke, Dupuis, and Lester<sup>4</sup> in their calculation of the high rotational states of the isotopomer  $H_2D^+$  in the electronic singlet state. Recent work by Carney *et al.*<sup>5</sup> is on the vibrational states of the isotopomers of singlet  $H_3^+$ .

The molecular ion  $H_3^+$  in its lowest electronic triplet state has attracted much less attention, mainly because no definite observation of its existence has been made to date. However, there are indications that it may exist in interstellar space and plasmas.<sup>6</sup> In order to make a definite statement about its existence, it is necessary to obtain its rovibrational "fingerprints." Since the calculation of molecular spectra of light systems has made enormous progress in the past decade, the prediction of such fingerprints by *ab initio* methods is now within reach.

The computation of the rovibrational spectra is usually based on the Born-Oppenheimer approximation, which divides the problem naturally into two steps. The first step consists of the solution of the electronic structure problem for a number of well-chosen nuclear geometries. These geometries must be chosen such that they allow a good—preferably an analytic—fit of the surface. The second step is the solution of the nuclear motion problem on the surface obtained in the first step.

This paper is concerned with the first step in the Born-Oppenheimer approximation: the generation of a PES that can be used in the solution of the nuclear motion problem. To that end more than 400 points on the PES of triplet  $H_3^+$  have been computed by the standard LCAO full CI technique. (Note that full CI for a two-electron system is the same as SDCl, i.e., configuration interaction based on singly and doubly excited states.) An analytic fit based on 240

points, systematically chosen by two numerical quadratures, is presented.

Although no computation of the full PES has been presented before, two different sets of *ab initio* computations on a number of geometries have appeared. Schaad and Hicks<sup>7</sup> found the ion to have an equidistant collinear structure and to be very weakly bound with respect to dissociation into an H atom and an  $H_2^+$  molecular ion. Their results were later confirmed by the more accurate calculations of Ahlrichs, Votava, and Zirz.<sup>8</sup>

These earlier calculations bring to light that the potential energy surface of  $H_3^+$  in the triplet state is very flat, so that the molecule is very floppy. Although the two papers just mentioned both gave interpretations of the vibrational spectrum that were based on a harmonic model and a single equilibrium structure, we believe that the molecule is not sufficiently rigid to warrant such an approach. In particular, we shall show that the energy barriers between the three structures  $H_2-H_1-H_3$ ,  $H_1-H_2-H_3$ , and  $H_1-H_3-H_2$  are so low that the protons tunnel easily between these symmetry-related minima. In the terminology of Longuet-Higgins<sup>9</sup> all the permutations of the protons are "feasible." Thus, it is necessary to treat the protons evenhandedly in the fit of the surface and the ensuing nuclear motion calculations.

A totally symmetric potential energy surface can be described in terms of a coordinate system first proposed by Smith<sup>10</sup> for the motion of three particles in a plane. Later Whitten and Smith<sup>11</sup> have extended this system to 3D motion. Basically, the coordinates are a hyperspherical form of the well known Jacobi coordinates.<sup>12</sup> Hyperspherical coordinates have a longer tradition in nuclear physics<sup>13,14</sup> than in molecular physics, although also in the latter field they have found numerous applications,<sup>15-23</sup> especially in the study of reactive three particle scattering. To our knowledge in all this work so far one has employed only model potentials. The present paper is an attempt to fit systematically an *ab initio* potential in terms of functions of the hyperspherical coordinates.

The Smith-Whitten coordinate system has been thoroughly discussed and somewhat modified by Johnson.<sup>16</sup> In the analytic fit of the surface we shall use a coordinate system that coincides to a large extent with Johnson's, but since the full use of permutation symmetry is important for us in keeping the required number of *ab initio* calculations to a mini-

imum, we give an alternative derivation of the necessary formulas that brings out more the role of permutation symmetry. Further we shall show that the coordinate system is nonorthogonal, i.e., it has a nondiagonal metric tensor, and discuss the choice of an appropriate set of expansion functions, which then is used in the representation of the PES. The fitted surface is presented in terms of expansion coefficients as well as contour plots.

## II. THE SMITH-WHITTEN HYPERSPHERICAL COORDINATES

In this section we define the coordinate system used in the fit of the potential energy surface (PES). The main purpose of this section is to give a self-contained account of the Smith-Whitten hyperspherical coordinates<sup>10,11</sup> and the way they behave under permutations of the particles. Although much of the theory presented in this and the next section can be found scattered in the literature,<sup>10,11,14-23</sup> it is embedded in many different formalisms and written in so many notations, that it is impossible to rely on a few references in the explanation of our representation of the PES.

The equations defining the hyperspherical coordinates can be presented very concisely in matrix language. To that end we write the matrices of proper, respectively improper, rotations as

$$\begin{aligned} \mathbf{R}(\omega) &:= \begin{pmatrix} \cos \omega & -\sin \omega \\ \sin \omega & \cos \omega \end{pmatrix}, \\ \mathbf{S}(\omega) &:= \begin{pmatrix} \cos \omega & \sin \omega \\ \sin \omega & -\cos \omega \end{pmatrix}. \end{aligned} \quad (1)$$

By a suffix we indicate a rotation axis, thus for instance a proper rotation around the  $z$  axis has the  $3 \times 3$  matrix:

$$\mathbf{R}_z(\omega) := \begin{pmatrix} \mathbf{R}(\omega) & \mathbf{0} \\ \mathbf{0}^T & \mathbf{1} \end{pmatrix}. \quad (2)$$

In an equivalent way the matrices  $\mathbf{R}_x(\omega)$ ,  $\mathbf{S}_z(\omega)$ , etc. are defined, which are matrices that properly, respectively improperly, rotate two axes, with a suffix indicating the third (invariant) axis.

Consider the coordinate (column) vectors  $\mathbf{x}_i$  of the protons in an arbitrary space-fixed frame. Since we are dealing with identical particles, it is convenient to assume that they have unit mass. Furthermore, we take the origin of the space-fixed frame in the center of mass of the system, so that  $\mathbf{x}_1 + \mathbf{x}_2 + \mathbf{x}_3 = \mathbf{0}$ . This restriction reduces the configuration space from the Euclidean space  $\mathbb{R}^9$  to its linear subspace  $\mathbb{R}^6$ . Defining the  $3 \times 3$  matrix  $\mathbf{X}$  by  $\mathbf{X} := (\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ , we can introduce Jacobi coordinates  $\mathbf{y}_i$ . This is done by means of a matrix  $\mathbf{T}$  acting on the right of  $\mathbf{X}$ . It is convenient to normalize the Jacobi coordinates, so that  $\mathbf{T}$  becomes orthogonal, thus,

$$\mathbf{Y} \equiv (\mathbf{y}_1, \mathbf{y}_2, \mathbf{0}) := \mathbf{X}\mathbf{T}, \quad (3a)$$

where

$$\mathbf{T} := \begin{pmatrix} \sqrt{\frac{2}{3}} & 0 & \sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{6}} & \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{3}} \\ -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{3}} \end{pmatrix}. \quad (3b)$$

The vectors  $\{\mathbf{y}_1 \oplus \mathbf{y}_2\}$  constitute the configuration space  $\mathbb{R}^6$ . If  $\mathbf{X}$  is of rank 1, i.e., the particles lie on a straight line, the two Jacobi vectors are linearly dependent.

The matrix  $\mathbf{X}$  spans a representation of the permutation group  $S_3$  as follows:

$$P(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = (\mathbf{x}_{p(1)}, \mathbf{x}_{p(2)}, \mathbf{x}_{p(3)}) = \mathbf{X}\mathbf{P}, \quad P \in S_3, \quad (4)$$

where  $\mathbf{P}$  is a  $3 \times 3$  matrix with unity in the position  $[p(i), i]$ ,  $i = 1, 2, 3$ , and zeros elsewhere. The matrix  $\mathbf{T}$  gives a decomposition of the rep of  $S_3$  spanned by  $\{\mathbf{x}_i\}$  into the irreducible representations (irreps)  $[2, 1]$  and  $[3]$  of  $S_3$ ,

$$P\mathbf{Y} = \mathbf{Y}\mathbf{T}^{-1}\mathbf{P}\mathbf{T} = \mathbf{Y} \begin{pmatrix} \mathbf{D}^{[2,1]}(P) & \mathbf{0} \\ \mathbf{0}^T & \mathbf{D}^{[3]}(P) \end{pmatrix}. \quad (5)$$

By virtue of the choice of  $\mathbf{T}$  this is a reduction into standard Young-Yamanouchi irreps<sup>24</sup> where, of course,  $\mathbf{D}^{[3]}(P) = 1$ . The even permutations in the irrep  $[2, 1]$  are represented by  $\mathbf{R}(k\frac{2\pi}{3})$ ,  $k = 0, 1, 2$ , with

$$(1) \rightarrow k = 0, \quad (123) \rightarrow k = 1, \quad (132) \rightarrow k = 2.$$

An odd permutation has the matrix  $\mathbf{S}(k\frac{2\pi}{3})$  with  $k$  given by

$$(23) \rightarrow k = 0, \quad (12) \rightarrow k = 1, \quad (13) \rightarrow k = 2.$$

In order to introduce the hyperspherical coordinates we need the diagonal matrix  $\mathbf{t}$  defined thus

$$\mathbf{t}(\frac{1}{2}\theta) := \begin{pmatrix} \cos(\frac{\theta}{2}) + \sin(\frac{\theta}{2}) & 0 & 0 \\ 0 & \cos(\frac{\theta}{2}) - \sin(\frac{\theta}{2}) & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (6)$$

Below it will be used that

$$\mathbf{t}(\frac{1}{2}\theta)^2 = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0}^T & \mathbf{0} \end{pmatrix} + \sin \theta \begin{pmatrix} \mathbf{S}(0) & \mathbf{0} \\ \mathbf{0}^T & \mathbf{0} \end{pmatrix}. \quad (7)$$

The six hyperspherical coordinates needed to cover  $\mathbb{R}^6$  are designated by  $r, \alpha, \beta, \gamma, \theta$ , and  $\phi$  and defined by

$$\mathbf{Y} =: \frac{r}{\sqrt{2}} \mathbf{R}_z(\alpha) \mathbf{R}_y(\beta) \mathbf{R}_z(\frac{1}{2}\gamma) \mathbf{t}(\frac{1}{2}\theta) \mathbf{R}_z(\frac{1}{2}\phi). \quad (8)$$

The fact that the angle  $\gamma$  appears here with a factor  $1/2$  is explained in the Appendix where  $\gamma, \theta$ , and  $\phi$  are shown to be simply related to  $SU(2)$  Euler angles. We shall show that the hyperspherical coordinates can be solved uniquely from Eq. (8) (except for a few exceptional points) provided we impose the following constraints:

$$\begin{aligned} r > 0, \quad 0 < \alpha < 2\pi, \quad 0 < \beta < \pi, \quad 0 < \gamma < 4\pi, \quad 0 < \theta < \frac{1}{2}\pi, \\ 0 < \phi < 2\pi. \end{aligned} \quad (9)$$

The hyperradius  $r$  is obtained thus,

$$\text{Tr}[\mathbf{Y}^T \mathbf{Y}] = |\mathbf{y}_1|^2 + |\mathbf{y}_2|^2 = \frac{1}{2} r^2 \text{Tr}[\mathbf{t}(\frac{1}{2}\theta)^2] = r^2, \quad (10)$$

where we cyclically permuted the orthogonal matrices under the trace. From Eqs. (5) and (10) it is immediately transparent that  $r$  is invariant under permutations. Further, we see that this coordinate is the radius of the sphere  $S^5$  in the space  $\mathbb{R}^6$  of the Jacobi vectors. The remaining five coordinates give a coordinate system for this hypersphere. In fact,  $S^5$  is a (Riemann) manifold, and the hyperspherical angles form a single chart. Strictly speaking, we need more than one

chart to cover the whole manifold, including the exceptional points, but we forego these mathematical subtleties.

Next we consider simultaneously  $\alpha$ ,  $\beta$ , and  $\theta$  and to that end we rewrite Eq. (8),

$$\mathbf{R}_y(-\beta)\mathbf{R}_z(-\alpha)\mathbf{Y} = \frac{r}{\sqrt{2}}\mathbf{R}_z(\frac{1}{2}\gamma)\mathbf{t}(\frac{1}{2}\theta)\mathbf{R}_z(\frac{1}{2}\phi). \quad (11)$$

On the left-hand side we find a rotation of the Jacobi vectors  $\mathbf{y}_1$  and  $\mathbf{y}_2$ . We can compute the vector product of these two vectors

$$\mathbf{y}_1 \times \mathbf{y}_2 = \sqrt{\frac{1}{12}}[2\mathbf{x}_1 - (\mathbf{x}_2 + \mathbf{x}_3)] \times [\mathbf{x}_2 - \mathbf{x}_3] \quad (12a)$$

$$= \sqrt{\frac{1}{3}}[\mathbf{x}_1 \times \mathbf{x}_2 + \mathbf{x}_2 \times \mathbf{x}_3 + \mathbf{x}_3 \times \mathbf{x}_1] \quad (12b)$$

$$= : \mathbf{N}. \quad (12c)$$

The vector  $\mathbf{N}$  is normal to the plane of the particles, and Eq. (12b) shows that  $\mathbf{N}$  transforms as the antisymmetric irrep [1<sup>3</sup>] of  $S_3$ . The vector product of the first two columns of  $\mathbf{t}(\frac{1}{2}\theta)\mathbf{R}(\frac{1}{2}\phi)$  equals  $(0, 0, \cos \theta)^T$ . Using the well-known result that a vector product transforms under proper rotations as a vector and equating the vector products obtained from the first two columns of the left- and right-hand sides of Eq. (11), we obtain

$$\begin{aligned} \mathbf{R}_y(-\beta)\mathbf{R}_z(-\alpha)\mathbf{N} &= \frac{1}{2}r^2\mathbf{R}_z(\frac{1}{2}\gamma)\begin{pmatrix} 0 \\ 0 \\ \cos \theta \end{pmatrix} \\ &= \frac{1}{2}r^2\begin{pmatrix} 0 \\ 0 \\ \cos \theta \end{pmatrix}. \end{aligned} \quad (13)$$

After expressing the normal  $\mathbf{N}$  in spherical polar coordinates  $N$ ,  $\theta_N$ ,  $\phi_N$ , we can easily verify that for  $\alpha = \theta_N$  and  $\beta = \phi_N$ , Eq. (13) becomes

$$\begin{pmatrix} 0 \\ 0 \\ N \end{pmatrix} = \frac{1}{2}r^2\begin{pmatrix} 0 \\ 0 \\ \cos \theta \end{pmatrix}, \quad (14)$$

where  $N \equiv |\mathbf{N}|$ . So,  $\alpha$  and  $\beta$  are the polar angles of  $\mathbf{N}$  and  $\theta$  is related to the length of  $\mathbf{N}$  by

$$\theta = \arccos\left(\frac{2N}{r^2}\right). \quad (15)$$

Evidently,  $0 < \alpha < 2\pi$ ,  $0 < \beta < \pi$ ,  $0 < \theta < \frac{1}{2}\pi$ . If  $\mathbf{y}_1$  and  $\mathbf{y}_2$  are linearly dependent  $\mathbf{N} = \mathbf{0}$  and  $\alpha$  and  $\beta$  are undetermined. This happens for a linear geometry of the molecule.

Since  $\mathbf{N}$  changes sign under odd permutations, it is clear that its polar angles behave under *odd* permutations as

$$\begin{aligned} \alpha &\rightarrow \alpha + \pi \\ &\Rightarrow \mathbf{R}_z(\alpha)\mathbf{R}_y(\beta) \rightarrow \mathbf{R}_z(\alpha)\mathbf{R}_y(\beta)\mathbf{R}_x(\pi) \\ \beta &\rightarrow \pi - \beta \end{aligned} \quad (16)$$

Under *even* permutations the angles  $\alpha$  and  $\beta$  are invariant, and  $\theta$ , being derived from  $N$ , is invariant under the whole group  $S_3$ .

The submanifold of  $S^5$ , characterized by constant  $\alpha$  and  $\beta$ , is the upper hemisphere of  $S^3$ , parametrized by  $\gamma$ ,  $\theta$ , and  $\phi$ , as is explained in the Appendix. This may be compared with the usual chart of  $S^2$ , formed by the spherical polars, where the submanifold of constant longitudinal angle, is the half-circle parametrized by the colatitude angle.

In order to find an equation for  $\phi$  we consider

$$\mathbf{Y}^T \mathbf{Y} = \frac{1}{2}r^2\mathbf{R}_z(-\frac{1}{2}\phi)\mathbf{t}(\frac{1}{2}\theta)^2\mathbf{R}_z(\frac{1}{2}\phi). \quad (17)$$

By use of Eq. (7) and by moving the part of this equation that is independent of  $\theta$  to the left-hand side of Eq. (17), we obtain for the nonzero  $2 \times 2$  block,

$$\begin{pmatrix} \frac{1}{2}(|\mathbf{y}_1|^2 - |\mathbf{y}_2|^2) & \mathbf{y}_1 \cdot \mathbf{y}_2 \\ \mathbf{y}_1 \cdot \mathbf{y}_2 & -\frac{1}{2}(|\mathbf{y}_1|^2 - |\mathbf{y}_2|^2) \end{pmatrix} = \frac{1}{2}r^2 \sin \theta \begin{pmatrix} \cos \phi & -\sin \phi \\ -\sin \phi & -\cos \phi \end{pmatrix}. \quad (18)$$

Hence,

$$r^2 \cos \phi \sin \theta = |\mathbf{y}_1|^2 - |\mathbf{y}_2|^2, \quad (19a)$$

$$r^2 \sin \phi \sin \theta = -2\mathbf{y}_1 \cdot \mathbf{y}_2, \quad (19b)$$

and  $\phi$  is determined uniquely in the interval  $0 < \phi < 2\pi$ . The point  $\theta = 0$  is an exceptional point of the coordinate system, it corresponds to an equilateral triangle.

With regard to the permutation property of  $\phi$  we observe that  $r$  and  $\theta$  are invariant and that  $\mathbf{y}_1$  together with  $\mathbf{y}_2$  spans the irrep [2,1]. Noting that  $S_3 \cong C_{3v}$ , we recall from elementary group theory that the pairs  $(x, y)$  and  $(x^2 - y^2, xy)$  both span the irrep  $E$  of  $C_{3v}$ . Translating this to the case at hand ( $x \rightarrow \mathbf{y}_1, y \rightarrow \mathbf{y}_2$ ), we find from Eq. (19) that the pair  $(\cos \phi, -\sin \phi)$  spans [2,1]. More specifically, one easily derives that, if  $P: \phi \rightarrow \phi'$ ,

$$\begin{aligned} (\cos \phi', -\sin \phi') &= (\cos \phi, -\sin \phi) \begin{cases} \mathbf{R}(2k\frac{2\pi}{3}) & \text{for even } P, \\ \mathbf{S}(2k\frac{2\pi}{3}) & \text{for odd } P. \end{cases} \end{aligned} \quad (20)$$

The permutation behavior of  $\phi$  is thus simply given by  $\phi' = (-1)^p(\phi + 2k\frac{2\pi}{3})$ , where  $(-1)^p$  is the parity of  $P$ .

To evaluate  $\gamma$ , finally, we introduce the matrix  $\mathbf{Z}$ ,

$$(\mathbf{z}_1, \mathbf{z}_2, \mathbf{z}_3) \equiv \mathbf{Z} = \mathbf{R}_y(-\beta)\mathbf{R}_z(-\alpha)\mathbf{Y}, \quad (21)$$

so that by Eq. (11),

$$\mathbf{Z}\mathbf{R}_z(-\frac{1}{2}\phi) = \frac{r}{\sqrt{2}}\mathbf{R}_z(\frac{1}{2}\gamma)\mathbf{t}(\frac{1}{2}\theta). \quad (22)$$

Multiplication of both sides from the right by the matrix  $(\theta \neq \frac{1}{2}\pi)$

$$\frac{1}{\cos \theta} \begin{pmatrix} \cos \frac{1}{2}\theta - \sin \frac{1}{2}\theta & 0 & 0 \\ 0 & \cos \frac{1}{2}\theta + \sin \frac{1}{2}\theta & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (23)$$

and equating the first column on the left- and right-hand side of the equation thus obtained, we get

$$\begin{aligned} &\begin{pmatrix} \cos \frac{1}{2}\gamma \\ \sin \frac{1}{2}\gamma \\ 0 \end{pmatrix} \\ &= \sqrt{2} \frac{\cos(\frac{1}{2}\theta) - \sin(\frac{1}{2}\theta)}{r \cos \theta} [\mathbf{z}_1 \cos(\frac{1}{2}\phi) - \mathbf{z}_2 \sin(\frac{1}{2}\phi)]. \end{aligned} \quad (24)$$

If  $\theta = \frac{1}{2}\pi$  the matrix  $\mathbf{t}(\frac{1}{2}\theta)$  becomes very simple and we can solve Eq. (22) directly. By application of L'Hospital's rule to Eq. (24) we obtain the same result for  $\theta = \frac{1}{2}\pi$ . So, Eq. (24) gives  $\gamma$  on the interval  $0 < \gamma < 4\pi$ .



The Jacobian (the root of the determinant of this tensor, the integration weight) is

$$|g|^{1/2} = \left(\frac{r}{2}\right)^5 \sin \beta \sin 2\theta. \quad (33)$$

It is seen that several off-diagonal elements are nonzero, and among them also  $g_{\phi\gamma}$ . If one were to apply some transformation to the external angle  $\gamma$  and the internal angle  $\phi$ , in order to orthogonalize these two coordinates, one would find that the PES depend on four coordinates, rather than on the minimum number three. In fact, orthogonal hyperspherical coordinate systems for real vector spaces of arbitrary dimension are well known (see, e.g., Ref. 25, pp. 302–307), but they do not give the required separation of the PES into external and internal coordinates.

It is also tedious to invert  $g$ . After several pages of computations of minors we find

$$\begin{aligned} g^{rr} &= 1, \\ g^{\alpha\alpha} &= \frac{1 + \cos \gamma \sin \theta}{\sin^2 \beta \cos^2 \theta} \frac{2}{r^2}, \\ g^{\beta\alpha} &= -\frac{\sin \gamma \sin \theta}{\sin \beta \cos^2 \theta} \frac{2}{r^2}, \\ g^{\beta\beta} &= \frac{1 - \cos \gamma \sin \theta}{\cos^2 \theta} \frac{2}{r^2}, \\ g^{\gamma\alpha} &= -\frac{(1 + \cos \gamma \sin \theta) \cos \beta}{\sin^2 \beta \cos^2 \theta} \frac{4}{r^2}, \\ g^{\gamma\beta} &= \frac{\cos \beta \sin \gamma \sin \theta}{\sin \beta \cos^2 \theta} \frac{4}{r^2}, \\ g^{\gamma\gamma} &= \left( \frac{2}{\sin^2 \theta} + \frac{4(1 + \cos \gamma \sin \theta) \cos^2 \beta}{\sin^2 \beta \cos^2 \theta} \right) \frac{2}{r^2}, \\ g^{\theta\theta} &= \frac{4}{r^2}, \\ g^{\phi\gamma} &= -\frac{\cos \theta}{\sin^2 \theta} \frac{4}{r^2}, \\ g^{\phi\phi} &= \frac{1}{\sin^2 \theta} \frac{4}{r^2}. \end{aligned} \quad (34)$$

The values of  $g^{-1}$  not shown are zero. Note that metric tensor and its inverse are not block-diagonal (except for  $r$  and  $\theta$ ), so that indeed the total tensor must be included in the inversion.

Substitution of Eqs. (33) and (34) into Eq. (31) gives the required kinetic energy (Laplace–Beltrami) operator  $\Delta$ . It can be shown (see Ref. 25, Chap. 15) that  $\Delta$  is the only Casimir operator of the orthogonal group SO(6). Compare this with SO(3), where there is also one Casimir operator (the usual angular momentum operator) and recall that the completeness of the eigenfunctions (the spherical harmonics) of this operator is proved by the Peter–Weyl theorem for SO(3).<sup>26</sup> In the same way as for SO(3) one proves from the Peter–Weyl theorem for SO(6) that the eigenfunctions of the angular part of  $\Delta$  form an orthogonal basis for the Hilbert space  $L^2(S^5)$ , consisting of square integrable functions on the sphere.

In the description of the PES we require functions that are independent of the external coordinates  $\alpha, \beta$ , and  $\gamma$ . This means that only the terms of  $\Delta$ , Eq. (31), have to be consid-

ered that depend on  $\theta$  and  $\phi$ . This part of the Laplace–Beltrami operator is

$$\nabla^2 = \left(\frac{2}{r}\right)^2 \left( \frac{1}{\sin 2\theta} \frac{\partial}{\partial \theta} \sin 2\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \quad (35)$$

Although this operator is similar in appearance to the usual angular momentum operator, there is the important difference that  $\sin 2\theta$  appears in the expression, rather than  $\sin \theta$ . This arises from the factor  $\sin 2\theta$  in the Jacobian, Eq. (33), and is consistent with the interval of  $\theta$ , i.e., the weight is positive on the interval.

The eigenvalue problem of  $\nabla^2$  can be separated in the manner, described in text books,<sup>27</sup> yielding the functions  $\exp(im\phi)$  in  $\phi$ , and for the variable  $\theta$  the equation

$$4\left(\frac{2}{r}\right)^2 \left[ \frac{1}{\sin \theta'} \frac{\partial}{\partial \theta'} \sin \theta' \frac{\partial}{\partial \theta'} - \left(\frac{m}{2}\right)^2 \frac{1 + \cos \theta'}{\sin^2 \theta'} \right] f_m(\theta') = A f_m(\theta'), \quad (36)$$

where  $\theta' := 2\theta$ . This is a well-known equation in the theory of the symmetric top and the representation theory of SU(2),<sup>26</sup> its solutions are the Wigner  $d$  functions  $d_{1/2m, -1/2m}^{(j)}(2\theta)$  with the corresponding eigenvalue  $A = -4j(j+1)(2/r)^2$ . The required expansion functions are finally (after the replacement  $\frac{1}{2}m \rightarrow m$ )

$$\begin{aligned} \chi_{jm}(\theta, \phi) &= \sqrt{\frac{2j+1}{2\pi}} d_{m, -m}^{(j)}(2\theta) e^{i2m\phi} \\ &= \sqrt{\frac{2j+1}{2\pi}} D_{m, -m}^{(j)}(0, 2\theta, 2\phi), \end{aligned} \quad (37)$$

where we have made the relation with the Wigner  $D$  matrix, defined in general as

$$D_{m, m}^{(j)}(\alpha, \beta, \gamma) := e^{-im\alpha} d_{m, m}^{(j)}(\beta) e^{-im\gamma}. \quad (38)$$

The normalization factor introduced in Eq. (37) normalizes the expansion functions to unity. Indeed, the  $\{\chi_{jm}\}$  are orthonormal with respect to the weight  $w(\theta, \phi) = \sin 2\theta$ , which can easily be proved by application of the orthogonality relation for SU(2) [not SO(3), because  $0 \leq 2\phi \leq 4\pi$ ]. Because the functions arise from a basis of  $L^2(S^5)$ , they are complete.

We want to stress that the functions with half-integer  $j$  must be included in order to achieve completeness. This can be easily shown by considering the simple function  $\cos \phi$ . It is readily seen that this function is orthogonal to all  $\chi_{jm}$ , with  $m \neq \pm 1/2$ , hence half-integer functions are required to describe  $\cos \phi$ .

#### IV. COMPUTATIONAL DETAILS

Each point on the electronic potential energy surface is computed by the standard LCAO-SCF-SDCI approach. The molecule H<sub>3</sub><sup>+</sup> being a two-electron system, SDCI is the same as full CI, so that the choice of a finite dimensional orbital basis is the major approximation in the calculation. As discussed in Sec. II, the PES depends on the hyperspherical coordinates  $\rho = r/\sqrt{2}$ ,  $\theta$ , and  $\phi$ . In order to find a reliable basis we first computed and fitted a part of the surface ( $\rho$  fixed at 2.5  $a_0$ ,  $\theta$  and  $\phi$  each running over five points) in a

large basis as a benchmark. This basis is an optimized Gaussian-type orbital (GTO) (10s, 4p, 1d/6s, 3p, 1d) basis. The quality of this basis may be judged by a computation on the <sup>2</sup>Σ<sub>g</sub> state of H<sub>2</sub><sup>+</sup> at R = 2.0 a<sub>0</sub>. Our value is 0.1 mhartree above the exact Born–Oppenheimer value<sup>28</sup> = 0.602 634 2 hartree, and 0.3 mhartree below a calculation by Ahlrichs *et al.*<sup>8</sup>

Secondly, we have computed and fitted the same part of the PES with a more modest uncontracted (5s, 3p) GTO basis. The exponents of the s orbitals are taken from Van Duijneveldt's compilation,<sup>29</sup> and those of the p orbitals from Ref. 4. The smaller basis gives energies on the grid of 25 points that are from 1.5 to 0.9 mhartree above the corresponding energies obtained in the large basis. This difference in energy is very uniform, and smaller than the errors introduced by the fit procedure.

The benchmark calculation shows that the smaller basis is quite reliable and since we are interested in a complete description of the PES, which requires many points, we decided to proceed with the 42-dimensional (5s, 3p) basis. The energy of H<sub>2</sub><sup>+</sup> in this basis is -0.602 014 7 hartree at a bond distance of 2.00 a<sub>0</sub>, and of the H atom it is -0.499 809 8, so that the dissociated complex has the energy -1.101 824 5 hartree.

In order to obtain the PES in the form of the expansion of Eq. (29), where the basis χ<sub>j<sub>m</sub></sub> is given in Eq. (37), we must calculate the integrals of Eq. (30), which are

$$C_{jm}(r) = \sqrt{\frac{2j+1}{2\pi}} \int_0^{(1/2)\pi} \int_0^{2\pi} d_{m,-m}^{(j)}(2\theta) e^{-2im\phi} E(r, \theta, \phi) \times \sin 2\theta d\theta d\phi. \quad (39)$$

Recall from Sec. II that the transposition (2,3) gives the map  $\phi \rightarrow -\phi$ . Since the PES  $E(r, \theta, \phi)$  is symmetric under this transposition, it follows that  $\sin 2m\phi$  drops out and only the term  $\cos 2m\phi$  in the exponential function survives the integration. Furthermore, we may restrict the  $\phi$  integration to the range  $0 < \phi < \pi$ , provided the integral is weighted by a factor 2. We also saw in Sec. II that even permutations give the substitution  $\phi \rightarrow \phi + k2\pi/3$ , which implies that only those terms  $\cos 2m\phi$  contribute that satisfy  $2m = 3n$ , where  $n$  is a natural number.

In order to prepare the integral of Eq. (39) for numerical quadrature we substitute

$$x = \cos 2\theta \quad \text{and} \quad y = \cos \phi \quad (40)$$

and rewrite the integral, thus,

$$C_{j,3n/2}(r) = \sqrt{\frac{2j+1}{2\pi}} \int_{-1}^1 \int_{-1}^1 G(r, x, y) \frac{dx dy}{\sqrt{1-y^2}}, \quad (41)$$

where

$$G(r, x, y) = d_{3n/2, -3n/2}^{(j)} [\arccos(x)] \cos[3n \arccos(y)] \times E[r, \frac{1}{2} \arccos(x), \arccos(y)]. \quad (42)$$

The integrals over  $x$  and  $y$  in Eq. (41) have the range and weight of, respectively, the Gauss–Legendre and the Gauss–Chebyshev quadrature.<sup>30</sup> Let us denote the grid points in  $x$  by  $x_\lambda$ ,  $\lambda = 1, \dots, N_x$ , and the corresponding weights by  $w_\lambda$ .

The Gauss–Chebyshev points are denoted by  $y_\mu$ ,  $\mu = 1, \dots, N_y$ , and in Ref. 30 we find that  $y_\mu = \cos \phi_\mu$  with  $\phi_\mu = [(2\mu - 1)/2N_y] \pi$ . Further we know that for all  $\mu$  the Gauss–Chebyshev weight is  $w_\mu = \pi/N_y$ . Thus, the integral in Eq. (41) is approximated by the following double sum:

$$C_{j,3n/2}(r) \approx \frac{\pi}{N_y} \sqrt{\frac{2j+1}{2\pi}} \sum_{\lambda=1}^{N_x} \sum_{\mu=1}^{N_y} w_\lambda d_{3n/2, -3n/2}^{(j)}(\theta_\lambda) \times \cos(3n\phi_\mu) E(r, \frac{1}{2} \theta_\lambda, \phi_\mu), \quad (43)$$

where  $\theta_\lambda = \arccos(x_\lambda)$ . After extensive numerical experimentation the number of points  $N_x$  in the  $\theta$  direction was chosen to be eight. Obviously, the larger this number the better the fit is, but the CI calculations necessary for the evaluation of  $E(r, \frac{1}{2} \theta_\lambda, \phi_\mu)$  form a limit on this number.

By the use of permutation symmetry a further reduction of the sum over  $\mu$  is possible, and to that end we choose the number of Gauss–Chebyshev points as a multiple of 3:  $N_y = 3K$ . Since the PES is invariant under the permutation (132) we find

$$E(r, \frac{1}{2} \theta_\lambda, \phi_{\mu+2K}) = E\left(r, \frac{1}{2} \theta_\lambda, \phi_\mu + \frac{2\pi}{3}\right) = E(r, \frac{1}{2} \theta_\lambda, \phi_\mu), \quad (44)$$

and it follows that the sum over  $\mu$  can be restricted to  $1 < \mu < 2K$ . Likewise from the invariance under the transposition (12),

$$E(r, \frac{1}{2} \theta_\lambda, \phi_{2K-\mu+1}) = E(r, \frac{1}{2} \theta_\lambda, -\phi_\mu + \frac{2\pi}{3}) = E(r, \frac{1}{2} \theta_\lambda, \phi_\mu). \quad (45)$$

Realizing that  $\mu = 1, \dots, 2K$  runs forwards and  $2K - \mu + 1$  runs backwards on the same grid, we find that the sum over  $\mu$  can be further restricted to  $1 < \mu < K$ . The grid  $\phi_\mu$ ,  $\mu = 1, \dots, K$ , covers equidistantly the interval  $[0^\circ, 60^\circ]$ . In the actual calculations we have chosen  $K = 5$ .

In summary, the fitted surface is based on 240 *ab initio* points: For six values of  $\rho$  we have computed the energies on an  $8 \times 5$  grid of  $\theta, \phi$  points. The  $\theta$  values are those belonging to an 8-point Gauss–Legendre quadrature and the  $\phi$  points belong to a 15-point Gauss–Chebyshev grid. Because of permutation symmetry only five points have to be calculated on the latter grid.

Since the electronic wave function calculated on a grid point depends parametrically on the nuclear coordinates, the operation of the nuclear permutations on the electronic wave function is well defined. A permutation yields a wave function belonging to a symmetry-related point of the potential energy surface. If the permutations do not coincide with point group operations, the six electronic wave functions obtained by the permutations are linearly independent. Accordingly, basis functions for all three irreps of  $S_3$  can be projected from a single electronic wave function.

In the second step of the Born–Oppenheimer approximation we must multiply a protonic wave function that transforms according to  $[\lambda]$ , where  $[\lambda]$  is one of the irreps of  $S_3$ , with a projected electronic wave function transforming according to the conjugate irrep  $[\bar{\lambda}]$ , in order to satisfy the Pauli principle for the protons. The protonic wave function itself contains a spatial and a spin part, which thus must be

combined to transform according to  $[\lambda]$ , which can be any of the three irreps of  $S_3$ , not just the antisymmetric one.

In the evaluation of the integral in Eq. (39) it is also necessary to compute the Wigner  $d$  functions  $d_{m,m'}^{(j)}(\beta)$ ,  $0 < \beta < \pi$ . Several recursion relations for these functions can be found in the literature, but some of these are not suitable for numerical computation. We have good experience with the following strategy for evaluating the matrix. If  $\frac{1}{2}\pi < \beta < \pi$  we first move this angle to the interval  $0 < \beta < \frac{1}{2}\pi$ , which is possible by virtue of the relation

$$d_{m,m'}^{(j)}(\pi - \beta) = (-1)^{j-m} d_{-m,-m'}^{(j)}(\beta). \quad (46)$$

Second, we divide out powers of  $\tan \frac{1}{2}\beta$  by defining (suppressing  $j$  in the notation)

$$t_{m,m'}(\beta) := d_{m,m'}(\beta) \tan^{m'-m}(\frac{1}{2}\beta). \quad (47)$$

For the function thus defined one derives easily the recursion relation

$$t_{-j,-j} = \cos^{2j}(\frac{1}{2}\beta)$$

and

$$t_{m,-j} = -\sqrt{\frac{j-m-1}{j+m}} t_{m-1,-j}, \quad (48)$$

from which the first (i.e., with index  $-j$ ) column can be computed. The next column is then obtained from

$$t_{m,-j+1} = \tan(\frac{1}{2}\beta) \left( \frac{-2j \cos \beta - 2m}{\sqrt{2j} \sin \beta} \right) t_{m,-j}, \quad (49)$$

and the remaining columns from

$$t_{m,m'} = [(j-m'+1)(j+m')]^{-1/2} \times \left\{ \tan(\frac{1}{2}\beta) \left( \frac{(m'-1)\cos \beta - m}{\sin \beta} \right) t_{m,m'-1} - [(j+m'-1)(j-m'+2)]^{1/2} \times \tan^2(\frac{1}{2}\beta) t_{m,m'-2} \right\}. \quad (50)$$

## V. RESULTS AND DISCUSSION

As discussed in Sec. IV, we have calculated eight energies for each value of  $\phi$  with  $\theta$  running over a Gauss-Legendre grid. Because an  $n$ -point Gaussian quadrature allows the integration of a polynomial of order  $2n-1$ , we can normalize numerically the expansion functions  $d_{m,-m}^{(j)}(\theta)$  up to and including  $j=15/2$ . For this reason we have truncated the expansion of the PES  $E(r,\theta,\phi)$ , cf. Eq. (29), at this  $j$  value. For a similar reason the  $\phi$  expansion in functions  $\cos m\phi$  has been truncated after five terms. Thus the expansion coefficients  $C_{jm}(r)$  are computed for  $j=0, 15/2$  ( $1/2$ ) and  $m=0, 6$  ( $3/2$ ). They are given in Table I for  $\rho := r/\sqrt{2} = 2, 2.5, 2.75, 3.0, 3.5$ , and  $4.0 a_0$ .

In Fig. 1 a 3D plot of the fitted surface at  $\rho = 2.5 a_0$  is presented. Note that this plot shows the *total* energy, i.e., the electronic *plus* the nuclear repulsion energy. At a glance we find a local minimum at the point  $(90^\circ, 60^\circ)$  in the  $\theta$ - $\phi$  plane. [From hereon we shall use the notation  $(\theta, \phi)$  to specify a point in this plane.] By the use of Eq. (27) it is readily seen that this point represents a linear, equidistant, geometry

TABLE I. Expansion coefficients  $C_{jm}(r)$ , cf. Eq. (30), as a function of  $\rho \equiv r/\sqrt{2} a_0$ .

$j$	$m$	2.0	2.5	2.75	3.0	3.5	4.0
0	0	-0.229 989 4(+1)	-0.208 223 1(+1)	-0.199 410 0(+1)	-0.191 693 6(+1)	-0.178 920 2(+1)	-0.168 892 8(+1)
1	0	0.224 994 4(+0)	0.217 039 5(+0)	0.212 077 8(+0)	0.206 775 3(+0)	0.195 486 8(+0)	0.183 600 6(+0)
$\frac{1}{2}$	$\frac{1}{2}$	0.102 111 1(+0)	0.108 869 9(+0)	0.110 944 5(+0)	0.112 345 6(+0)	0.113 402 8(+0)	0.112 459 2(+0)
2	0	-0.407 932 6(-1)	-0.504 854 3(-1)	-0.541 126 6(-1)	-0.570 749 0(-1)	-0.614 508 1(-1)	-0.643 053 6(-1)
$\frac{3}{2}$	$\frac{3}{2}$	-0.298 065 5(-1)	-0.349 063 8(-1)	-0.368 405 2(-1)	-0.384 360 1(-1)	-0.408 734 0(-1)	-0.426 472 5(-1)
3	0	0.258 071 3(-1)	0.281 850 5(-1)	0.291 108 3(-1)	0.298 815 3(-1)	0.310 026 1(-1)	0.317 157 7(-1)
3	3	-0.194 505 5(-1)	-0.233 051 6(-1)	-0.248 312 0(-1)	-0.261 010 0(-1)	-0.279 861 9(-1)	-0.292 847 8(-1)
$\frac{7}{2}$	$\frac{7}{2}$	0.138 068 8(-1)	0.168 753 9(-1)	0.181 701 1(-1)	0.193 080 9(-1)	0.211 217 6(-1)	0.223 826 9(-1)
4	0	-0.562 345 9(-2)	-0.887 842 6(-2)	-0.102 871 5(-1)	-0.115 521 8(-1)	-0.136 774 8(-1)	-0.152 952 6(-1)
4	3	0.909 109 9(-2)	0.114 814 4(-1)	0.125 287 6(-1)	0.134 858 7(-1)	0.151 313 7(-1)	0.163 893 4(-1)
$\frac{5}{2}$	$\frac{5}{2}$	-0.597 029 2(-2)	-0.778 608 5(-2)	-0.858 135 5(-2)	-0.931 013 0(-2)	-0.105 985 0(-1)	-0.116 763 9(-1)
$\frac{3}{2}$	$\frac{3}{2}$	0.624 432 0(-2)	0.805 271 1(-2)	0.885 496 6(-2)	0.960 052 7(-2)	0.109 368 3(-1)	0.120 509 7(-1)
5	0	0.650 589 2(-2)	0.737 790 1(-2)	0.775 861 6(-2)	0.811 564 2(-2)	0.876 858 7(-2)	0.935 536 1(-2)
5	3	-0.441 770 4(-2)	-0.583 950 9(-2)	-0.645 570 7(-2)	-0.701 668 6(-2)	-0.800 227 8(-2)	-0.884 285 2(-2)
$\frac{11}{2}$	$\frac{11}{2}$	0.336 428 8(-2)	0.448 015 3(-2)	0.496 621 3(-2)	0.541 105 4(-2)	0.618 446 8(-2)	0.682 815 8(-2)
$\frac{7}{2}$	$\frac{7}{2}$	-0.317 073 7(-2)	-0.428 668 8(-2)	-0.477 393 2(-2)	-0.521 721 6(-2)	-0.598 690 8(-2)	-0.663 338 7(-2)
6	0	-0.102 312 1(-2)	-0.217 973 2(-2)	-0.268 827 6(-2)	-0.315 077 5(-2)	-0.394 911 2(-2)	-0.460 161 9(-2)
6	3	0.233 116 7(-2)	0.322 121 7(-2)	0.361 513 5(-2)	0.397 692 8(-2)	0.462 160 6(-2)	0.516 708 3(-2)
6	6	-0.208 883 4(-2)	-0.285 086 9(-2)	-0.318 903 9(-2)	-0.349 737 4(-2)	-0.402 886 6(-2)	-0.446 732 3(-2)
$\frac{13}{2}$	$\frac{13}{2}$	-0.145 832 6(-2)	-0.207 424 1(-2)	-0.235 278 2(-2)	-0.260 893 0(-2)	-0.306 704 7(-2)	-0.346 554 3(-2)
$\frac{9}{2}$	$\frac{9}{2}$	0.167 658 2(-2)	0.236 686 3(-2)	0.267 699 4(-2)	0.296 116 7(-2)	0.347 270 4(-2)	0.391 326 8(-2)
7	0	0.154 954 5(-2)	0.178 317 1(-2)	0.189 563 6(-2)	0.199 909 0(-2)	0.218 354 8(-2)	0.235 793 2(-2)
7	3	-0.111 690 8(-2)	-0.158 863 2(-2)	-0.180 295 7(-2)	-0.199 873 9(-2)	-0.234 250 7(-2)	-0.264 028 4(-2)
7	6	0.109 307 3(-2)	0.155 288 7(-2)	0.176 551 1(-2)	0.196 117 4(-2)	0.230 664 9(-2)	0.261 029 7(-2)
$\frac{15}{2}$	$\frac{15}{2}$	0.626 552 9(-3)	0.856 455 9(-3)	0.964 150 3(-3)	0.106 182 0(-2)	0.122 197 0(-2)	0.135 827 3(-2)
$\frac{11}{2}$	$\frac{11}{2}$	-0.831 294 7(-3)	-0.120 908 1(-2)	-0.137 962 7(-2)	-0.153 718 5(-2)	-0.181 488 4(-2)	-0.205 047 6(-2)

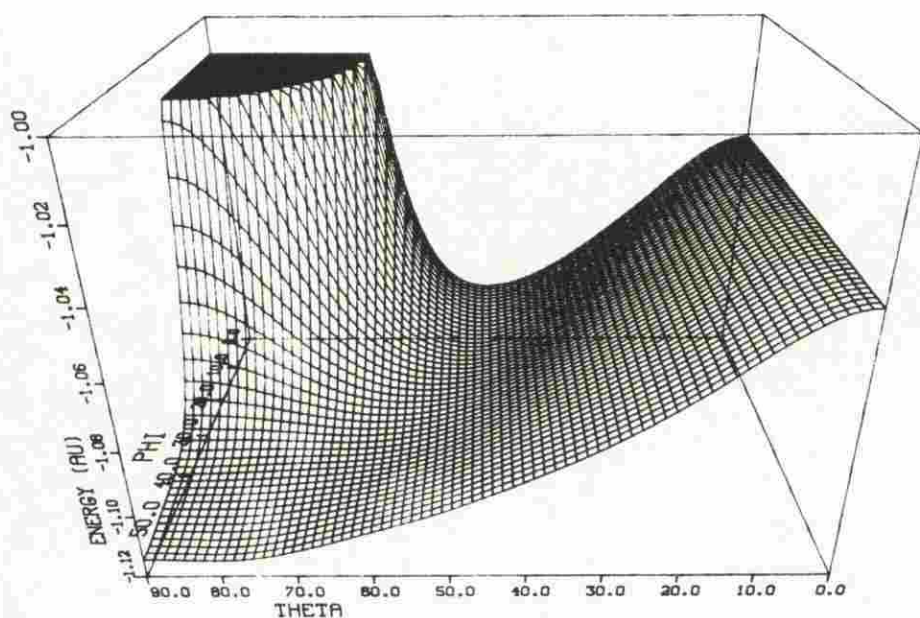


FIG. 1. Surface of total energy for  $\rho = 2.5 a_0$ . The minimum occurs for  $\phi = 60^\circ$ ,  $\theta = 90^\circ$ ; an equidistant linear structure close to the absolute minimum.

with interatomic distances of  $2.5 a_0$  ( $= \rho$ ). In order to locate more precisely the absolute minimum, we performed a number of additional CI calculations, and found this minimum to be of energy  $-1.11466$  hartree and to occur for a linear geometry with interatomic distances  $|\mathbf{x}_1 - \mathbf{x}_2| = |\mathbf{x}_2 - \mathbf{x}_3| = 2.45 a_0$ . The binding energy with respect to  $H_2^+$  and H is 12.84 mhartree. Schaad and Hicks<sup>7</sup> found  $2.457 a_0$  and 12.16 mhartree for these values. The most accurate numbers are those of Ahlrichs *et al.*<sup>8</sup>:  $2.457 a_0$  and 14.43 mhartree, respectively.

Quite noticeable in Fig. 1 is the peak at  $(90^\circ, 0^\circ)$ , where atoms 2 and 3 coincide and atom 1 is at a distance  $\sqrt{3}\rho$  from the coinciding pair. The presence of this Coulomb singularity in the  $\theta$ - $\phi$  plane is the reason that we fitted the electronic energy and added the nuclear repulsion afterwards.

Another feature to be observed is the saddle point at  $(44.4^\circ, 0^\circ)$ . This point corresponds to a T-shaped van der Waals type complex consisting of a slightly compressed  $H_2^+$  unit (bond distance  $1.94 a_0$ ) and the H-atom 1 at a distance of  $3.99 a_0$  from this molecular ion. Recalling from Sec. II that the plane  $\phi = 0$  is a symmetry plane corresponding to the transposition (2,3), we see that the point  $(90^\circ, -60^\circ)$  belongs to the linear molecule 2-3-1. Hence the saddle point is the "transition state" of the "reaction" 1-2-3  $\rightarrow$  2-3-1. For this reason we pinpointed the saddle point somewhat more accurately by performing some extra CI calculations and found a barrier energy of 11.78 mhartree ( $= 2585 \text{ cm}^{-1}$ ) belonging to a T-shaped complex consisting of equilibrium  $H_2^+$  and atom 1 at a distance  $4.5 a_0$ . Obviously the binding in this complex is mainly due to monopole/induced-dipole interaction. The depth of the van der Waals well is 1.06 mhartree. The height of the barrier being of the same order of magnitude as the first vibrational transition<sup>31</sup> in  $H_2^+$  ( $2297 \text{ cm}^{-1}$ ) we find a large likelihood of tunneling between the symmetry-related minima. Ahlrichs *et al.*<sup>8</sup> found  $1233 \text{ cm}^{-1}$  for the largest harmonic vibrational frequency of triplet  $H_3^+$ .

A final remark to be made about Fig. 1 is that we see a valley, extending from the minimum to the saddle point, that runs more or less along a circle with an origin at  $(90^\circ, 0^\circ)$ . This is seen more clearly in Fig. 2, which is a contour version of Fig. 1. The same sort of circular valleys, but with decreasing radii, are observed in the contour plots of Figs. 4-7. Figure 3 gives the surface at  $\rho = 2.0 a_0$ .

In order to explain the occurrence of these valleys we recall that the (normalized) Jacobi coordinates are designated by  $y_1$  (a vector pointing from the midpoint of the atom pair 2-3 to 1) and  $y_2$ , which is a vector pointing from atom 3 to 2. Except for the normalization, the vectors  $y_1$  and  $y_2$  are the atom-diatom coordinates usually designated by  $\mathbf{R}$  and  $\mathbf{r}$ , respectively. Let  $\xi$  be the angle between these vectors, then from Eqs. (12) and (13) we find

$$d \sin \xi = \cos \theta, \quad (51)$$

and from Eq. (19b),

$$d \cos \xi = -\sin \phi \sin \theta, \quad (52)$$

with

$$d = \frac{2y_1 y_2}{r^2}, \quad -1 \leq d < 1. \quad (53)$$

For fixed  $d$  Eqs. (51) and (52) define a curve  $[\theta(\xi), \phi(\xi)]$  in the  $\theta$ - $\phi$  plane. The endpoints of the curve are

$$[\theta(\pi), \phi(\pi)] = [\frac{1}{2}\pi, \arcsin(d)] \quad (54)$$

and

$$[\theta(\frac{1}{2}\pi), \phi(\frac{1}{2}\pi)] = [\frac{1}{2}\pi - \arcsin(d), 0]. \quad (55)$$

Hence, the curve  $[\theta(\xi), \phi(\xi)]$  intercepts the  $\phi = 0^\circ$  axis at the same value as the  $\theta = 90^\circ$  axis, from which it can be surmised that the curve is more or less circular. It can be shown that the smaller the radius  $\arcsin(d)$  the more circular the curve is, whereas for larger  $d$  it bulges somewhat around  $\xi \approx 135^\circ$ .

In the neighborhood of  $y_2 \equiv \frac{1}{2}\sqrt{2}|\mathbf{x}_2 - \mathbf{x}_3| = \frac{1}{2}\sqrt{2} 2.0 a_0$



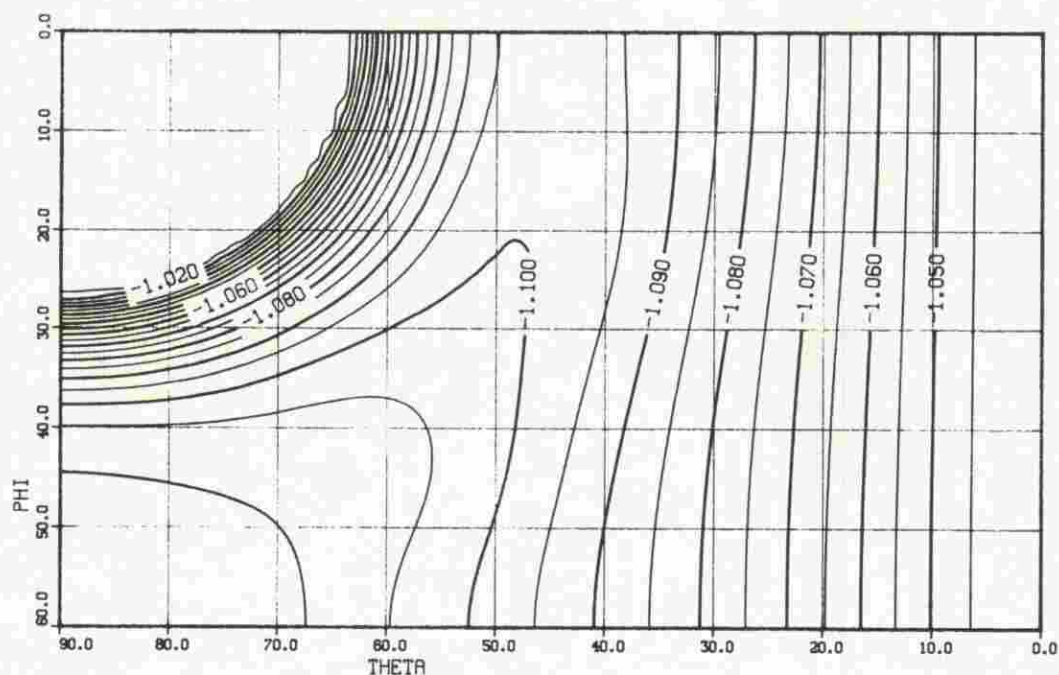


FIG. 2. A contour plot of Fig. 1, i.e., the surface at  $\rho = 2.5 a_0$ .

the PES will show a valley due to the chemical bonding in  $H_2^+$ . Since in the contour plots of Figs. 2–7 the hyperradius  $r$  is kept constant, this means that we may expect a dip in the energy along an approximately circular path of radius

$$\arcsin(d) = \arcsin\left(2.0 \frac{\sqrt{2r^2 - 4.0}}{r^2}\right), \quad (56)$$

corresponding to a varying atom-diatom angle  $\pi > \xi > \frac{1}{2}\pi$  and a constant  $H_2^+$  equilibrium bond distance. This is indeed observed in the plots.

Outside this circular region, where the  $H_2^+$  bond is broken, we have a system of two separate atoms and a proton, bound by induction and dispersion forces. For the larger  $\rho$  values the greater part of the contour plots describe the dissociated system, whereas for the smaller  $\rho$  values a good part of the plots pertain the bonding in  $H_2^+$ . Since  $\theta$  and  $\phi$  depend on the inverse of the hyperspherical radius  $r \equiv \sqrt{2}\rho$ , as follows from Eq. (27), the width of the valley decreases with increasing  $r$ . So, for large  $r$  we find a narrow circular gorge of a small radius  $\arcsin(d)$ , Eq. (56), surrounding an infinite peak due to nuclear repulsion. Outside this gorge

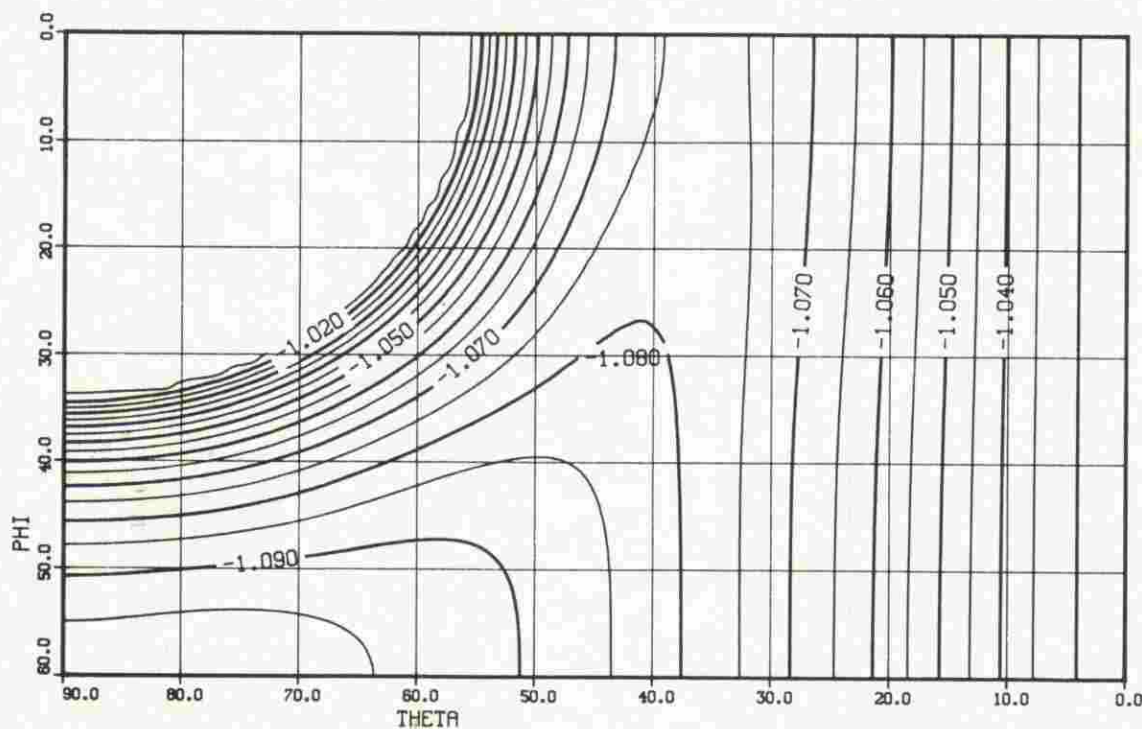


FIG. 3. Contour plot of the total energy for  $\rho = 2.0 a_0$ . The minimum for  $\theta = 90^\circ$  and  $\phi = 60^\circ$  corresponds to a collinear structure.

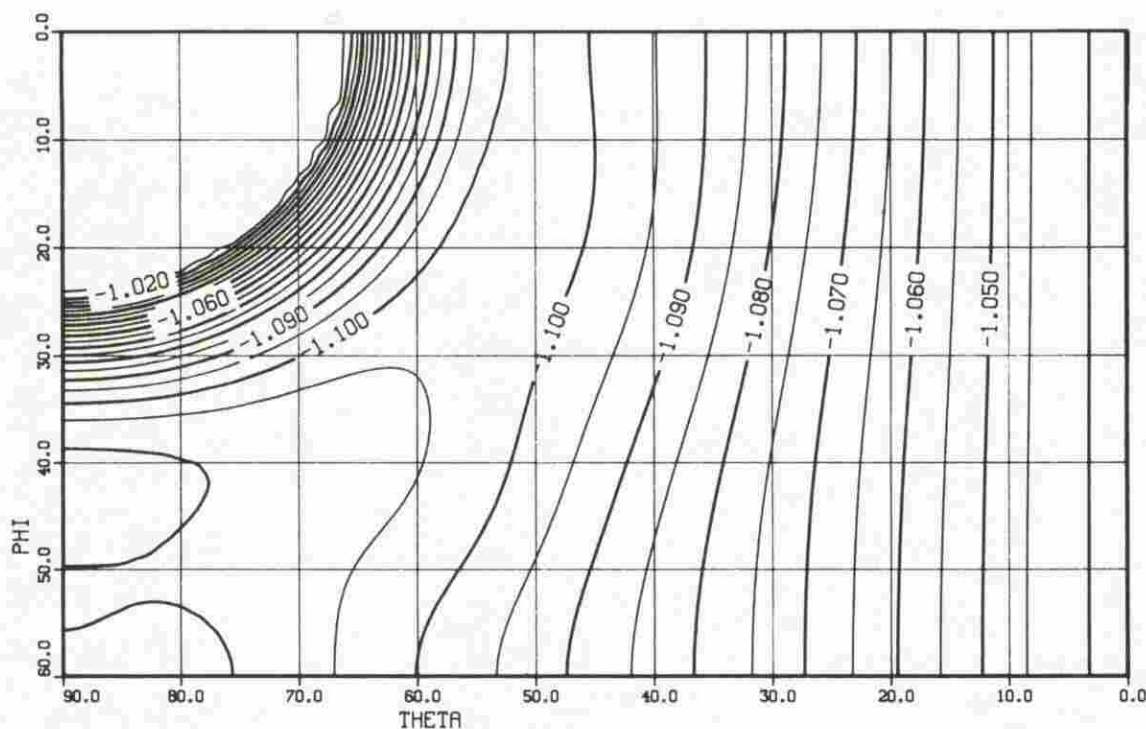


FIG. 4. Contour plot of the total energy for  $\rho = 2.75 a_0$ . The minimum for  $\theta = 90^\circ$  and  $\phi = 60^\circ$  corresponds to a collinear structure. A secondary minimum appears for a linear van der Waals complex  $H_2^+ - H$ .

variations in energy are due to van der Waals forces which are several orders of magnitude smaller than the binding energy of  $H_2^+$ , and so this part of the surface is flat.

The quadrature points, sampling the surface, have been chosen independent of  $r$ , and so the gorge can be missed easily for the larger hyperradii. Indeed, initially we tried to fit also an asymptotic surface for  $\rho = 10.0 a_0$ , but this turned out to be impossible. However, for the smaller hyperradii, too,

the quality of the fit is somewhat disappointing, as may be judged from the values in Table II. (We are able to present this table because our first attempts to describe the PES were based on  $5 \times 5$  grids, and an expansion in spherical harmonics. The corresponding quadrature points being different from the ones used in the present fits, the earlier results are useful as a check on the accuracy of the fit.) Table II confirms that the quality of the fit deteriorates with increasing  $r$ .

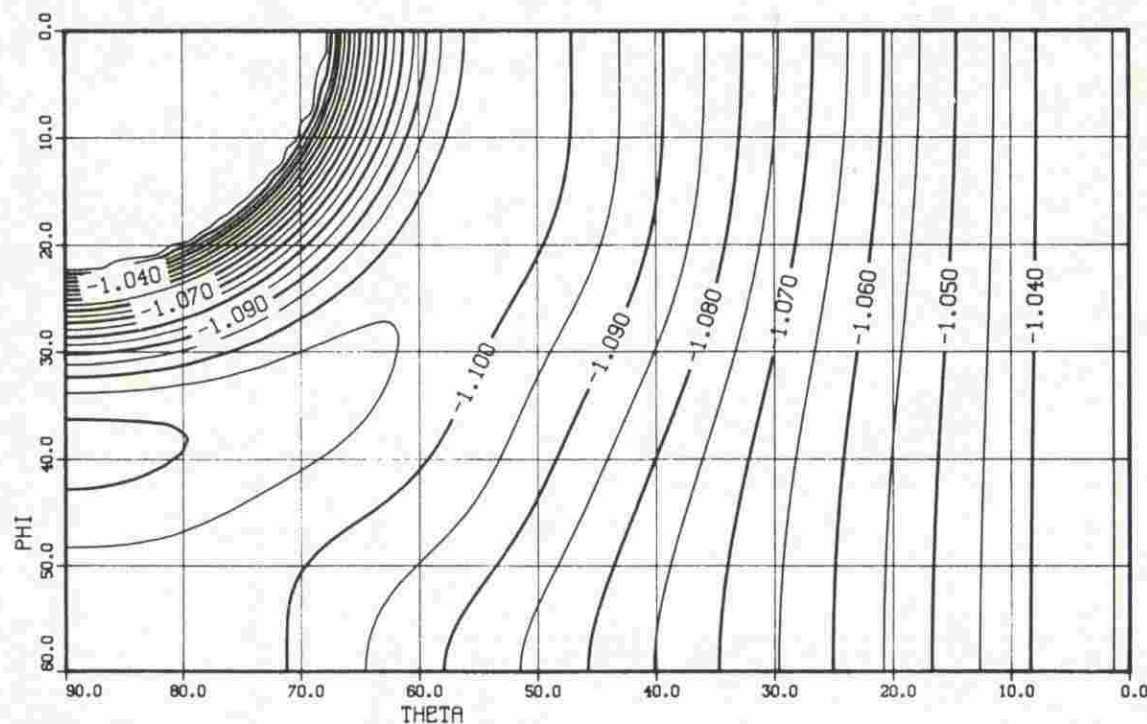


FIG. 5. Contour plot of the total energy for  $\rho = 3.0 a_0$ . The minimum for  $\theta = 90^\circ$  corresponds to a linear van der Waals complex  $H_2^+ - H$ .

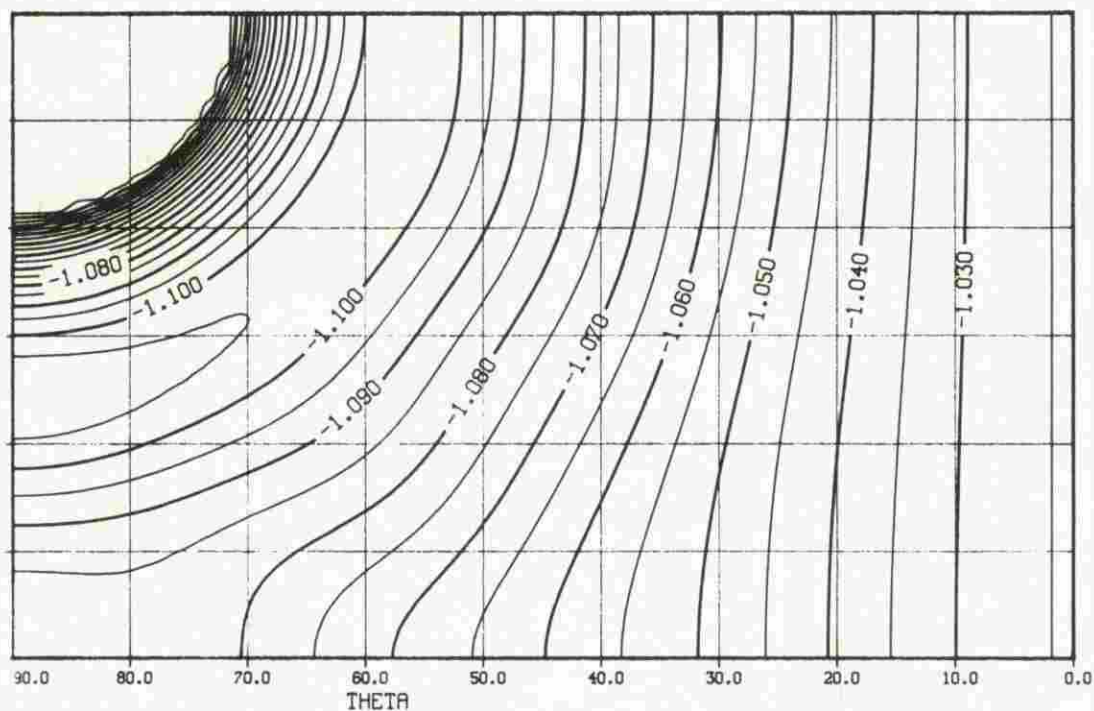


FIG. 6. Contour plot of the total energy for  $\rho = 3.5 a_0$ . The minimum for  $\theta = 90^\circ$  corresponds to a linear van der Waals complex  $H_2^+ - H$ .

## VI. SUMMARY AND CONCLUSIONS

We have seen that the Smith-Whitten hyperspherical coordinates form a coordinate system for  $R^6$  that has well-defined properties under permutations of the particles. Hence it is possible to define totally symmetric functions of these coordinates. Such functions can be used to describe the potential energy surfaces of systems of three identical particles. Furthermore, the Smith-Whitten coordinates have the advantage that they divide into two groups: three external

coordinates that give the orientation of the system in space and three internal coordinates  $r$ ,  $\theta$ , and  $\phi$  that define the geometry of the system.

In order to obtain the potential energy surface of  $H_3^+$  in its lowest triplet state the set of  $D$  matrices  $D_{m,-m}^{(j)}$  ( $0, 2\theta, 2\phi$ ) was introduced, and the PES is expanded in terms of these functions.

From this work it becomes apparent that the use of hyperspherical coordinates is not without problems. Especially for larger values of the hyperradius  $r$ , the fit of the surface is

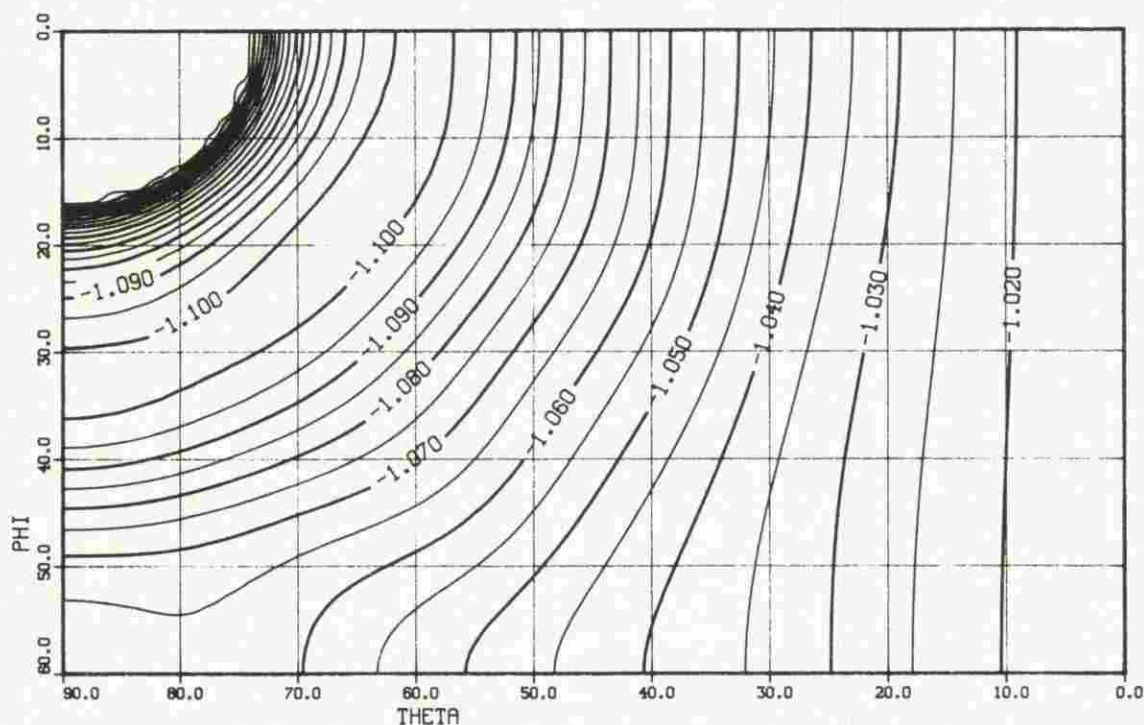


FIG. 7. Contour plot of the total energy for  $\rho = 4.0 a_0$ . The van der Waals complex  $H_2^+ - H$ , with H circling the molecule-ion, is the circular valley between the  $-1.100$  hartree lines.

TABLE II. Quality of the fits obtained from  $8 \times 5$  grids in comparison with values computed in  $5 \times 5$  grids. Root mean square and maximum deviation in mhartree,  $\rho \equiv r/\sqrt{2} a_0$ .

	$\rho = 2.0$	$\rho = 2.5$	$\rho = 2.75$	$\rho = 3.0$	$\rho = 3.5$	$\rho = 4.0$
rms	0.08	0.10	0.12	0.13	0.16	0.18
$\Delta E_{\max}$	1.16	1.82	2.10	2.36	2.86	3.27

not as good as may be hoped for. The main reason for this is that the effects due to the chemical bonding in  $H_2^+$  give rise to a narrow gorge in the surface that is otherwise very flat. The description of such a narrow gorge requires long expansions and many CI calculations. Even if one is prepared to compute these long expansions, it remains to be seen how useful they will be in variational dynamics calculations, since they will require likewise long expansions for the wave function of the nuclei.

Although the present surface does not have spectroscopic accuracy, it is better than many of the existing model three-body potentials. Until better potential energy surfaces become available, it can be of use in semiquantitative nuclear motion calculations.

Finally, it must be remarked that hyperspherical coordinates are nonorthogonal. Since this nonorthogonality gives rise to many cross derivatives in the kinetic energy operator, a dynamics calculation in terms of these coordinates will be a major undertaking, even if high accuracy surfaces become available.

#### ACKNOWLEDGMENTS

The authors thank Dr. J. Tennyson for suggesting the problem and Professor B. T. Sutcliffe, Professor A. van der Avoird, and Professor J. Hougen for critically reading the manuscript.

#### APPENDIX

We shall show that the hyperspherical angles  $\gamma$ ,  $\theta$ , and  $\phi$  are, in fact, the Euler angles of the special unitary group  $SU(2)$ . Consider to that end Eq. (22) of the main text. The nonzero  $2 \times 2$  block appearing in that equation satisfies the relation

$$\begin{pmatrix} z_{11} & z_{12} \\ z_{21} & z_{22} \end{pmatrix} = \frac{r}{\sqrt{2}} \left\{ \cos \frac{1}{2} \theta \mathbf{R} \left[ \frac{1}{2} (\gamma + \phi) \right] + \sin \frac{1}{2} \theta \mathbf{R} \left[ \frac{1}{2} (\gamma - \phi) \right] \mathbf{S}(0) \right\}. \quad (\text{A1})$$

Perform the following rotation on the column vector  $(z_{11}, z_{21}, z_{12}, z_{22})^T$ :

$$\begin{pmatrix} \alpha_0 \\ \alpha_1 \\ \alpha_2 \\ \alpha_3 \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 0 & 1 \\ 0 & -1 & -1 & 0 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} z_{11} \\ z_{21} \\ z_{12} \\ z_{22} \end{pmatrix} = r \begin{pmatrix} \cos \frac{1}{2} \theta \cos \frac{1}{2} (\gamma + \phi) \\ -\sin \frac{1}{2} \theta \sin \frac{1}{2} (\gamma - \phi) \\ \sin \frac{1}{2} \theta \cos \frac{1}{2} (\gamma - \phi) \\ \cos \frac{1}{2} \theta \sin \frac{1}{2} (\gamma + \phi) \end{pmatrix}. \quad (\text{A2})$$

For a hyperradius  $r = 1$  the parameters  $\{\alpha_i\}$  are the Euler-Rodrigues parameters<sup>32</sup> of  $SU(2)$ . By the use of Eq. (2.21) of Ref. 32 they are related to the usual Euler angles. In this case this relationship becomes

$$\begin{pmatrix} \alpha_0 - i\alpha_3 & -\alpha_2 - i\alpha_1 \\ \alpha_2 - i\alpha_1 & \alpha_0 + i\alpha_3 \end{pmatrix} = r \begin{pmatrix} e^{-i(\gamma/2)} & 0 \\ 0 & e^{i(\gamma/2)} \end{pmatrix} \times \begin{pmatrix} \cos \frac{1}{2} \theta & -\sin \frac{1}{2} \theta \\ \sin \frac{1}{2} \theta & \cos \frac{1}{2} \theta \end{pmatrix} \begin{pmatrix} e^{-i(\phi/2)} & 0 \\ 0 & e^{i(\phi/2)} \end{pmatrix}. \quad (\text{A3})$$

This equation shows that, for hyperradius  $r = 1$ ,  $\gamma$ ,  $\theta$ , and  $\phi$  are the parameters of  $SU(2)$ .

It is known that  $SU(2)$  as a differentiable manifold is homeomorphic to the sphere  $S^3$  in four space. Much confusion has existed about the domain of its parameters. This confusion has been cleared up by Jonker and De Vries,<sup>33</sup> who showed that for

$$0 < \gamma < 4\pi, \quad 0 < \theta < \pi, \quad 0 < \phi < 2\pi \quad (\text{A4})$$

the sphere is covered exactly once. In the present case the range of  $\theta$  is  $0 < \theta < \frac{1}{2}\pi$ , so that only the upper hemisphere of  $S^3$  is covered.

In his original paper<sup>10</sup> Smith considered a 2D model, i.e., he constrained the motion of the particles to a plane. After we separate off the center of mass,  $R^4$  becomes the configuration space of the 2D model. Clearly, the  $SU(2)$  Euler angles and the hyperradius  $r$  form a coordinate system for this space. By the Peter-Weyl theorem the Wigner-matrix elements  $D_{mm}^{(j)}(\gamma, \theta, \phi)$  form a complete set on  $S^3$ , and restricting these functions to a subset that is independent of  $\gamma$ , we find the spherical harmonics. Hence, in the 2D model it is reasonable and consistent to expand the PES in terms of spherical harmonics. Initially we pursued that line of approach, but found that spherical harmonics do not represent the surface as well as the  $D$  functions used in the main text. For instance, for  $\rho = 4.0 a_0$  we find a rms error of 0.608 mhartree and a maximum deviation from the 25 reference points of 14.16 mhartree. As can be seen in Table II, the corresponding numbers for the  $D$  functions are considerably better.

<sup>1</sup>T. Oká, Phys. Rev. Lett. **45**, 531 (1980).

<sup>2</sup>W. Meyer, P. Botschwina, and P. Burton, J. Chem. Phys. **84**, 891 (1986).

<sup>3</sup>J. Tennyson and B. T. Sutcliffe, Mol. Phys. **85**, 1067 (1986).

<sup>4</sup>R. Schinke, M. Dupuis, and W. A. Lester, Jr., J. Chem. Phys. **72**, 3909 (1980).

<sup>5</sup>G. D. Carney, S. M. Adler-Golden, and D. C. Leskeski, J. Chem. Phys. **84**, 3921 (1980).

<sup>6</sup>J. Tennyson (private communication).

<sup>7</sup>L. J. Schaad and W. V. Hicks, J. Chem. Phys. **61**, 1934 (1974).

<sup>8</sup>R. Ahlrichs, C. Votava, and C. Zirz, J. Chem. Phys. **66**, 2771 (1977).

<sup>9</sup>H. C. Longuet-Higgins, Mol. Phys. **6**, 445 (1963).

<sup>10</sup>F. T. Smith, J. Math. Phys. **3**, 735 (1962).

<sup>11</sup>R. C. Whitten and F. T. Smith, J. Math. Phys. **9**, 1103 (1968).

<sup>12</sup>E. T. Whittaker, *Analytical Dynamics of Particles and Rigid Bodies*, 4th ed. (Cambridge University, Cambridge, 1965), pp. 348-351.

<sup>13</sup>W. Zickendraht, Ann. Phys. **35**, 18 (1965).

<sup>14</sup>R. C. Whitten and J. S. Sims, Phys. Rev. A **9**, 1586 (1974).

<sup>15</sup>A. Kuppermann, Chem. Phys. Lett. **32**, 374 (1975).

<sup>16</sup>B. R. Johnson, J. Chem. Phys. **73**, 5051 (1980).

<sup>17</sup>M. Mishra and J. Linderberg, Mol. Phys. **50**, 91 (1983).

- <sup>18</sup>M. Mishra, J. Linderberg, and Y. Öhrn, *Chem. Phys. Lett.* **111**, 439 (1984).
- <sup>19</sup>J. Linderberg and Y. Öhrn, *Int. J. Quantum Chem.* **27**, 273 (1985).
- <sup>20</sup>R. T Pack and G. A. Parker, *J. Chem. Phys.* **87**, 3888 (1987).
- <sup>21</sup>V. Aquilanti and S. Cavalli, *J. Chem. Phys.* **85**, 1355 (1986).
- <sup>22</sup>V. Aquilanti, S. Cavalli, and G. Grossi, *J. Chem. Phys.* **85**, 1362 (1986).
- <sup>23</sup>J. G. Frey and B. J. Howard, *Chem. Phys.* **99**, 415 (1985).
- <sup>24</sup>M. Hamermesh, *Group Theory and its Application to Physical Problems* (Addison-Wesley, Reading, MA, 1962), p. 224.
- <sup>25</sup>A. O. Barut and R. Raczka, *Theory of Group Representations and Applications* (PWN, Warszawa, 1977).
- <sup>26</sup>J. D. Talman, *Special Functions. A Group Theoretic Approach* (Benjamin, New York, 1968), Chaps. 8 and 9.
- <sup>27</sup>H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand, Princeton, 1956), Chap. 7.
- <sup>28</sup>J. M. Peek, *J. Chem. Phys.* **43**, 3004 (1965).
- <sup>29</sup>F. B. Van Duijneveldt, IBM Report No. RJ945, San José, CA, 1971.
- <sup>30</sup>*Handbook of Mathematical Functions*, edited by M. Abramowitz and L. A. Stegun (U.S. GPO, Washington, D.C., 1964), p. 887.
- <sup>31</sup>G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, 1950).
- <sup>32</sup>L. C. Biedenharn and J. D. Louck, *Angular Momentum in Quantum Physics* (Addison-Wesley, Reading, MA, 1981).
- <sup>33</sup>J. E. Jonker and E. De Vries, *Nucl. Phys. A* **105**, 621 (1967).

The Journal of Chemical Physics is copyrighted by the American Institute of Physics (AIP). Redistribution of journal material is subject to the AIP online journal license and/or AIP copyright. For more information, see <http://ojps.aip.org/jcpo/jcpcr/jsp>  
Copyright of Journal of Chemical Physics is the property of American Institute of Physics and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.