An accurate analytic H_4 potential energy surface: EPAPS appendices

A. I. Boothroyd, P. G. Martin, and W. J. Keogh*
Canadian Institute for Theoretical Astrophysics, University of Toronto, Toronto, Ontario, M5S 3H8, Canada

M. J. Peterson†
Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 3H6, Canada
(August 3, 2001: J. Chem. Phys., in press)

Abstract

This electronic submission to EPAPS contains appendices detailing matters of restricted interest. The modified Schaefer/Köhler surface used to generate $H_2 + H_2$ conformations is described in detail. The Gaussian basis set is described, and small corrections to the MRD-CI *ab initio* H_4 energies are discussed. The conical intersection of the H_4 ground state with the first excited state is discussed, and the position of this conical intersection is mapped out over a large fraction of the H_4 conformation space. Additional plots of the new BMKP analytic H_4 surface are presented, showing some additional comparisons of the surface with *ab initio* energies.

APPENDIX A: MODIFIED SCHAEFER/KÖHLER FORMULA

The Schaefer and Köhler[1] formula was used to generate high-accuracy energies to constrain our fitted surface in the $H_2 + H_2$ van der Waals region. Their formula was designed only for an equilibrium H_2 molecule size of 1.449 a_0; however, non-equilibrium H_2 sizes were also needed to constrain our analytic H_4 surface. We thus considered H_2 molecules of sizes chosen from $\{0.6, 0.8, 1.0, 1.2, 1.449, 1.75, 2.1, 2.6, 3.4\ a_0\}$, but with fewer intermolecular distances and fewer orientations for sizes other than 1.449 a_0 (and lower weight in the fit). Our *ab initio* energies indicated that the position of the van der Waals well

---

*Present address: i-STAT Canada Ltd., 436 Hazeldean Road, Kanata, Ontario, K2L 1T9, Canada.

†Present address: Department of Computing and Networking Services, University of Toronto, Toronto, Ontario, M5S 3J1, Canada.

and its repulsive wall varied with the size of the H_2 molecules; to approximate this effect, the Schaefer and Köhler[1] formula was modified slightly, such that its repulsive wall joined smoothly onto that from the *ab initio* energies. The original Schaefer and Köhler[1] surface is written in terms of functions of the intermolecular separation R multiplied by functions of the orientation angles θ_1, θ_2, and ϕ, where $\cos\theta_1 = \vec{r}_a \cdot \vec{R}/(r_a R)$, $\cos\theta_2 = -\vec{r}_b \cdot \vec{R}/(r_b R)$, and $\cos\phi = (\vec{r}_a \times \vec{R}) \cdot (\vec{r}_b \times \vec{R})/(|\vec{r}_a \times \vec{R}||\vec{r}_b \times \vec{R}|)$. The original formula was modified in two ways.

(i) The modified Schaefer/Köhler formula which takes into account molecules with non-equilibrium separation was constructed by replacing R in their equations with a shifted value

$$R_{sk} = R + 0.4 \max\{0.0\ a_0\,,\ 2.8\ a_0 - (r_a + r_b)\} - 1.0 \max\{0.0\ a_0\,,\ D_{eq} - D\}\,, \tag{A1}$$

where D is the shortest of the distances from an atom (or from the mid-point of an H_2 molecule) to the closest point on the line segment joining the atoms of the other H_2 molecule, and D_{eq} is defined as follows. If $\max\{r_a, r_b\} \leq 1.5\ a_0$, then $D_{eq} \equiv D$. Otherwise, for the same orientation and separation R, consider a reference case in which the two H_2 molecules have a size of 1.5 a_0 (slightly above the equilibrium separation); D_{eq} is defined to be the value of D for this reference case. Thus the first shift in equation (A1) applies for small molecules, and the second shift for large molecules (provided that the molecules are angled at least somewhat toward each other). Note that conformations were discarded altogether if the shortest distance B between atoms in different molecules was too small, namely, $B < 3.5\ a_0$ for $r_a = r_b = 1.449\ a_0$, $B < 4\ a_0$ for $1.2\ a_0 \leq \{r_a, r_b\} \leq 1.75\ a_0$, $B < 5\ a_0$ for $\max\{r_a, r_b\} = 3.4\ a_0$, and $B < 4.5\ a_0$ otherwise.

(ii) For small molecules, the anisotropic part of the Schaefer/Köhler surface was reduced, leaving the isotropic part unchanged, so that small molecules behave as if they were more nearly spherical. This was accomplished by applying reduction factors f_1 and f_2 to the anisotropic terms:

$$\begin{aligned} V_{sk} \; = \; & V_{000}(R_{sk}) \\ & + f_1 f_2 [a_{220} V_{220}(R_{sk}) + a_{222} V_{222}(R_{sk}) + a_{224} V_{224}(R_{sk})] \\ & \qquad \times \sin^2\theta_1 \sin^2\theta_2 \cos 2\phi \\ & + f_1 f_2 [b_{220} V_{220}(R_{sk}) + b_{222} V_{222}(R_{sk}) + b_{224} V_{224}(R_{sk})] \\ & \qquad \times \cos\theta_1 \cos\theta_2 \sin\theta_1 \sin\theta_2 \cos\phi \\ & + f_1 f_2 [c_{220} V_{220}(R_{sk}) + c_{222} V_{222}(R_{sk}) + c_{224} V_{224}(R_{sk})] \\ & \qquad \times [1.5\cos^2\theta_1 - 0.5][1.5\cos^2\theta_2 - 0.5] \\ & + d_{202} V_{202}(R_{sk})\,(f_1[1.5\cos^2\theta_1 - 0.5] + f_2[1.5\cos^2\theta_2 - 0.5]) \end{aligned} \tag{A2}$$

where the reduction factors f_1 and f_2 are given by

$$f_1 = \min\{1.0\,,\ r_a/(1.449\ a_0)\} \qquad \text{and} \qquad f_2 = \min\{1.0\,,\ r_b/(1.449\ a_0)\} \tag{A3}$$

(and $a_{220}, \ldots, d_{202}$ are constants in the Schaefer/Köhler formula obtained from Clebsch-Gordan coefficients and from the definitions of spherical harmonics as a function of θ and ϕ). Note that Diep and Johnson[2] computed rigid-rotor $H_2 + H_2$ potentials for H_2 molecule sizes of both 1.449 a_0 and 1.402 a_0; their figures 11 and 12 suggest that the latter case is slightly less anisotropic, in qualitative agreement with our above assumption.

Note that this modified version of the Schaefer/Köhler formula does not have continuous derivatives and is thus not suited for use as an actual H_4 surface. In addition, since no information was available to us on how the depth of the van der Waals well might change for non-equilibrium H_2 molecules, we had to assume that the depth of the van der Waals well was independent of the H_2 molecule size (and simply give lower weight in the fit to van der Waals points generated with non-equilibrium H_2 molecules). However, this modified formula is adequate for generating constraining conformations at discrete distances, to give a general guide as to the position of the van der Waals well for our H_4 fit.

APPENDIX B: THE MRD-CI CALCULATIONS

1. The Gaussian basis set used

As in our earlier work[3], we used the same $(9s3p1d)/[4s3p1d]$ Gaussian basis set as Siegbahn and Liu[4], with 19 basis functions per hydrogen atom, yielding 76 basis functions in all for H_4. For purposes of testing the basis correction, Boothroyd *et al.*[3] used the $(9s3p)/[4s3p]$ basis set obtained by omitting the d-function; for testing H_3, Boothroyd *et al.*[3] also used a $(9s3p2d)/[4s3p2d]$ Gaussian basis set, which was obtained by taking the $(9s3p)/[4s3p]$ basis set and adding two d-functions, with exponents optimized to a few μE_h in complete CI calculations on the H_2 molecule at a separation of 1.4 a_0. These basis sets are presented below in Table I, along with the $(8s2p1d)/[4s2p1d]$ basis set used by Schwenke[5,6].

2. Small corrections to the MRD-CI energies

Using different basis sets, different SCF types, different configuration selection thresholds, and/or different CI reference sets for a given H_4 conformation yielded MRD-CI energies that differed systematically, though by relatively small amounts. Extrapolation to zero threshold (performed automatically by the MRD-CI program) and the Davidson correction to full CI are both standard procedures. The London-type basis correction is reasonably well justified, and makes a significant improvement in the accuracy. In addition, we made two small ad hoc corrections (detailed below), functions of the extrapolation threshold and the SCF type, to improve consistency among the various cases; these latter two corrections were typically smaller than the random errors in the energies, and could have been omitted with only minor effect on the final energy values.

a. Correction to the extrapolation to zero threshold

The systematic energy differences between three different CI configuration selection thresholds were used to estimate a small ad hoc systematic correction (i.e., a small modification to the MRD-CI program's extrapolation to zero threshold). Most of the single-root energies had a configuration selection threshold of $T = 10$ μE_h (referred to as "$T10$" cases) and/or $T = 2$ μE_h ("$T2$"), and a few hundred also had $T = 0.4$ μE_h ("$T.4$");

the multiple-root energies were $T10$, with $T2$ also computed for a few hundred conformations. The MRD-CI program used the truncated-CI energies $E(T)$ and $E(2T)$ to obtain an extrapolated energy $E_{ex} \equiv E_\lambda(T) \equiv E_\lambda(2T)$. The size of the resulting extrapolation $\Delta E_{ex}(T) \equiv E(T) - E_{ex}$ to zero threshold averaged about 9.6, 3.1, and 1.1 mE_h, respectively, for single-root $T10$, $T2$, and $T.4$ cases (somewhat less for multiple-root cases); estimated extrapolation uncertainties were roughly 0.5, 0.2, and 0.1 mE_h, respectively. A slightly improved extrapolation is possible[3] using $E_\lambda(3T)$ and $E_\lambda(4T)$ (which were also computed, and give some indication of the non-linearity of the extrapolation), by adding a correction of $-0.25\Delta_{34}$, where $\Delta_{34} \equiv E_\lambda(3T) + E_\lambda(4T) - 2E_{ex}$. Since the extrapolation to zero threshold is generally quite linear, this correction was small: it had an rms size of 0.09, 0.04, and 0.02 mE_h, respectively, for $T10$, $T2$, and $T.4$ cases, and reduced the rms difference between 1753 cases with differing thresholds from 0.42 to 0.41 mE_h. In a manner similar to Boothroyd *et al.*[3], consistency between different threshold cases could be significantly improved (rms difference reduced from 0.41 to 0.30 mE_h) by adding an ad hoc systematic correction Δ_T as a function of the size of the extrapolation:

$$\Delta_T = \mu^{(\mathrm{SCF})} \max\{\, f_\nu^{(T)} \Delta_{min} \,,\, \min[\, \Delta E_{ex}(T) \,,\, f_\nu^{(T)} \Delta_{max} \,] \,\} - f_\nu^{(T)} \nu^{(\mathrm{SCF})} \quad , \tag{B1}$$

where $\mu^{(\mathrm{SCF})} = 0.13$, 0.065, and 0.06 and $\nu^{(\mathrm{SCF})} = 0.87$, 0.072, and 0.15 mE_h, for closed, open, and mixed SCF cases, respectively; $f_\nu^{(T)} = 3/2$, $1/2$, and $1/6$ for $T10$, $T2$, and $T.4$ cases, respectively; $\Delta_{min} = 1.5\ mE_h$ and $\Delta_{max} = 10.5\ mE_h$. The rms size of this correction was 0.42, 0.13, and 0.06 mE_h, respectively, for $T10$, $T2$, and $T.4$ cases (comparable to the size of the estimated errors in the extrapolation to zero threshold, and somewhat smaller than the total estimated uncertainties).

b. SCF-type correction

Small but not completely negligible systematic differences were found in energies computed using molecular orbitals from different SCF types. Consistency could be improved significantly by applying a small ad hoc correction, estimated by comparing MRD-CI energies computed using different SCF types. Since closed shell SCF is expected to be best suited to describe H_4, the correction Δ_{SCF} was applied (as a function of H_4 geometry) to the open and mixed shell cases (in a manner similar to Boothroyd *et al.*[3]):

$$\begin{aligned} \Delta_{\mathrm{SCF}} = {} & -\kappa^{(\mathrm{SCF})} \cos\left(2\pi \min\left\{ \frac{p - 2.35\ a_0}{7.35\ a_0} \,,\, \frac{5}{4} \right\}\right) \exp\left(-\frac{p - 2.35\ a_0}{4.6\ a_0}\right) \\ & - \eta^{(\mathrm{SCF})} f_\nu^{(T)} \max\left\{ 1 - \frac{p}{4\ a_0} \,,\, 0 \right\} \quad , \end{aligned} \tag{B2}$$

where p is the sum of the sizes of the "best H_2 molecules" (i.e., the sum of the two end-segments of the shortest non-branching path connecting the four H atoms); $\kappa^{(\mathrm{SCF})} = 0.65$ and 0.60 mE_h for open and mixed shell SCF, respectively; $\eta^{(\mathrm{SCF})} = 0.60\ mE_h$ for open shell SCF, vanishing for mixed shell; and $f_\nu^{(T)}$ is as defined above for Δ_T. This is the most ad hoc of the corrections, but it was applied to relatively few points (since most points used closed-shell SCF). The rms size of this correction was 0.26 and 0.23 mE_h for open and mixed shell SCF, respectively; it reduced the differences rms(closed – open) from 0.60 to 0.44 mE_h (698 cases), rms(closed – mixed) from 0.48 to 0.42 mE_h (527 cases), and rms(open – mixed) from 0.31 to 0.28 mE_h (672 cases). (Both the corrections and the improvements in the rms differences are larger for small p, i.e., for compact geometries.) These rms differences give an estimate of the combined "random" errors introduced by the extrapolation to zero threshold and the correction to full CI.

APPENDIX C: POSITION OF THE H_4 CONICAL INTERSECTION

Since our highest-symmetry *ab initio* points were among the first ones to be computed with multiple roots, it soon became clear that the ground state and the first excited state were degenerate for most equilateral-pyramid conformations (three atoms in an equilateral triangle, with the fourth atom directly above the center — C_{3v} symmetry). Shifting the position of the fourth atom from the center-line of the equilateral base, or distorting the shape of the base, lifts the degeneracy. The H_4 London equation exhibits a cusp as one passes through an equilateral-pyramid geometry, just as the H_3 London equation has a cusp at the conical intersection equilateral-triangle H_3 conformations. Another similarity between H_4 and H_3 is an "anomaly" at small sizes. Multiple-root *ab initio* energies computed at compact geometries for the BKMP2 H_3 PES[7] demonstrated that sufficiently small equilateral triangles ceased to represent conical intersections of the H_3 ground and excited states (the non-degenerate A_1' root dips below the degenerate E' roots at small sizes). In the H_4 surface, for equilateral pyramids with base sizes smaller than 2 a_0 a similar thing happens for some pyramid heights, as shown in Figure 1. The region of conformation space where equilateral pyramids do *not* have a degenerate ground state energy (and thus do not lie on the conical intersection with the first excited state) is shown in Figure 2.

In contrast to the H_3 surface, for the H_4 surface the conical intersection between ground state and first excited state is by no means confined to conformations with C_{3v} symmetry. When we looked at the worst points in one of our earlier fits, we found that many of them were on or near conical intersections. However, in general the London equation either had a cusp nearby but in the wrong position, or had no cusp in the vicinity at all — this was what was leading to the large errors relative to the *ab initio* energies. We went to some effort to map out the positions of the conical intersection, in the hopes that it might be simple enough to incorporate into the fitted surface. Unfortunately, the conical intersection turns out to lie on a rather complicated 3-dimensional hypersurface in the 6-dimensional conformation space of H_4. Mapping out a reasonable portion of the conical intersection required computation of 13356 *ab initio* points (with multiple roots).

We characterize the conical intersection as follows. Let two H-atoms lie on the z-axis equidistant from the origin, with separation r_1 (note that r_1 need not be the shortest distance in the conformation). Let the third atom lie on the y-axis, at a position y_3. Let the fourth atom lie in the x-y plane, at a distance x_4 from the the y-z plane defined by atoms one through three. Then there may be zero, two, four, or six positions y_4 of the fourth atom that lie on the conical intersection — which thus may be mapped out as a function of three of these four coordinates r_1, y_3, x_4, and y_4. It is not completely certain that such geometries can characterize the *entire* conical intersection, particularly for smaller geometries where a different excited state can intersect with the ground state (e.g., the "anomalous" region discussed above, a cut through which is shown in Fig. 2); mapping out the conical intersection in complete detail is beyond the scope of this paper.

Figure 3 illustrates the position of the conical intersection for planar conformations, at six values of the coordinate r_1. Formally, the conical intersection continues out towards infinity while asymptotically approaching the dotted lines (i.e., approaching an equilateral triangle with a fourth atom approaching $\pm\infty$ along the triangle's line of reflection symmetry — at infinity, this yields the H_3 conical intersection). Note the qualitative difference in shape at the smallest r_1 value — as r_1 is reduced from 2.1 to 1.75 a_0, the two nearly-horizontal solid lines forming a "funnel-shape" at $r_1 = 2.1\ a_0$ presumably move closer together and pinch off near $y_3 = 3\ a_0$ to yield the closed curve plus "cup-on-its-side" shape at $r_1 = 1.75\ a_0$. Although it is not obvious from Figure 3, we have checked that in fact squares are *not* on the conical intersection (at least for squares with sides longer than 1 a_0), though they can be close enough to show a local "bump" in the energy as one passes through a square geometry.

Figure 4 illustrates the position of the conical intersection for non-planar conformations at a value of $r_1 = 2.6\ a_0$, in terms of the position of the fourth atom in the x-y plane for various values of the position y_3 of the third atom. For $y_3 = 0$, the first three atoms form a straight line on the z-axis, and the conical intersection lies on a circle in the x-y plane centered at the origin. As y_3 is increased, a bulge pushes out of the right-hand side of this locus and grows larger; the left-hand side shifts rightwards somewhat and eventually flattens out. At some point (between $y_3 = 1.5$ and 1.6 a_0), a "bean-shaped" locus also appears farther to the left, and grows larger as y_3 increases. As y_3 approaches the equilateral-triangle position $y_3 = r_1\sqrt{2}/3 = 2.251666\ a_0$, the right-hand side of the original locus moves off to infinity, leaving a vertical locus along that defined by the apexes of equilateral pyramids; the left-hand side of the "bean-shaped" locus moves off to minus infinity, while its right-hand side approaches the vertical line of the original locus except for a fair-sized "bubble" around $x_4 = 0$. As y_3 increases beyond the equilateral-triangle position, the point $(x_4 = \pm\infty, y_4 \approx y_3)$ where the two loci touch moves in rapidly from infinity, yielding a single "distorted oval" locus around the origin. As y_3 is increased towards infinity, this oval grows wider until it approaches a circle of radius $r_1\sqrt{2}/3$ centered on the origin, i.e., with the fourth atom forming an equilateral triangle with the first two atoms — the H_3 conical intersection again.

Figure 5 illustrates the conical intersection for non-planar conformations at a somewhat smaller value of $r_1 = 2.1\ a_0$. The behavior is qualitatively similar; however, if one reduced r_1 below $\sim 2\ a_0$, the behavior would change qualitatively, as is clear from Figures 2 and 3.

Figure 6 illustrates the conical intersection for non-planar conformations at a large value of $r_1 = 4.0\ a_0$. There is a qualitative difference from smaller r_1 values, in that there is no second "bean-shaped" locus; as y_4 passes through the equilateral-triangle position, the original locus (grown infinitely large to the right) "flips over" to the left and shrinks back down from infinity. However, this qualitative difference is to some extent an artifact of the choice of coordinates. If, instead of choosing cuts in the planes $y_3 =$ constant, one had chosen to look at cuts in the planes $y_3 - y_4 =$ constant, the behavior would be qualitatively similar for all $r_1 \gtrsim 2\ a_0$ (as may be seen by considering cuts parallel to the dashed lines in Fig. 3).

We have given an overview of the geometry of the position of the H_4 conical intersection. Given the complexity of the geometry of the conical intersection, providing a *full* characterization of its geometry is beyond the scope of this paper.

APPENDIX D: MORE OF THE SURFACES' WORST FEATURES

This section contains three additional figures, further illustrating some of the "wiggles" in the fitted analytic surfaces relative to the *ab initio* energies.

Figure 7 shows a case (small $r_a = 0.8\ a_0$, large $r_b = 5.0\ a_0$, with small intermolecular separations R) where the adopted 400-parameter surface "Ad" does somewhat better than either the 785-parameter surface "A" from which it was obtained or the best surface without London cusp-rounding "G" (especially for "parallel" orientations). Note that the energy plotted on the vertical axis is the $H_2 + H_2$ interaction energy for the given H_2-molecule sizes, i.e., the total energy E minus the energy E_{ref} of separated molecules of sizes r_a and r_b. The energy scale of this plot is expanded enough that errors of order 1 mE_h in the *ab initio* energies are clearly visible by comparing a point to its neighbors. Note that the plots shown here contain extra-closely-spaced *ab initio* points for illustrative purposes, that were not included in the set of fitted points.

Figure 8 shows an example of a case ($r_a = 1.4\ a_0$, $r_b = 3.4\ a_0$) where surfaces "Ad" and "A" are completely smooth at the places where the surface "G" (without London cusp-rounding) has spurious cusps of order 20 mE_h (at $R \sim 1.2$ and 1.1 a_0, respectively, for "Y-shape" and "crossed" orientations of the H_2 molecules).

Figure 9 presents an example of an $H_3 + H$ case, showing not only the ground state *ab initio* energies but also the first and second excited state energies (though the second excited state lies offscale for this figure). It is a T-shaped conformation based on a linearly symmetric H_3. The energy scale on the vertical axis is the interaction energy between a single H atom and a linear symmetric H_3 which has the given interatomic separations $A = B$. In Figure 9, all three surfaces "Ad", "A", and "G" do about equally well in fitting a conical intersection, since in this case the surface "G" has no London cusp.

REFERENCES

[1] J. Schaefer and W. E. Köhler, Z. Phys. **D 13**, 217 (1989).
[2] P. Diep and J. K. Johnson, J. Chem. Phys. **112**, 4465 (2000).
[3] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. J. Peterson, J. Chem. Phys. **95**, 4331 (1991).
[4] P. Siegbahn and B. Liu, J. Chem. Phys. **68**, 2457 (1978).
[5] D. W. Schwenke, J. Chem. Phys. **89**, 2076 (1988).
[6] D. W. Schwenke, private communication (1989).
[7] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, J. Chem. Phys. **104**, 7139 (1996).

TABLES

TABLE I. The Gaussian basis sets.

Our basis sets[a]			Schwenke's basis set[b]		
Type	Exponent ($a_0{}^{-2}$)	Coefficient	Type	Exponent ($a_0{}^{-2}$)	Coefficient
s	837.22	0.000112	s	402.0099	0.000198
	123.524	0.000895		60.24196	0.001531
	27.7042	0.004737		13.73217	0.007919
	7.82599	0.019518		3.904505	0.031747
	2.56504	0.065862		1.282709	0.100619
	0.938258	0.178008			
s	0.372145	1.0	s	0.465544	1.0
s	0.155838	1.0	s	0.181120	1.0
s	0.066180	1.0	s	0.072791	1.0
p	2.1175	1.0	p	1.5	1.0
p	0.77	1.0	p	0.375	1.0
p	0.28	1.0			
d	1.0	1.0	d	1.0	1.0
d[c]	1.76	1.0			
d[c]	0.62	1.0			

[a]The $(9s3p1d)/[4s3p1d]$ basis set was taken from Siegbahn and Liu[4].
[b]Schwenke's $(8s2p1d)/[4s2p1d]$ basis set: see Refs. 5 and 6.
[c]This pair of d-functions replaces the single d-function, to get the $(9s3p2d)/[4s3p2d]$ basis set.

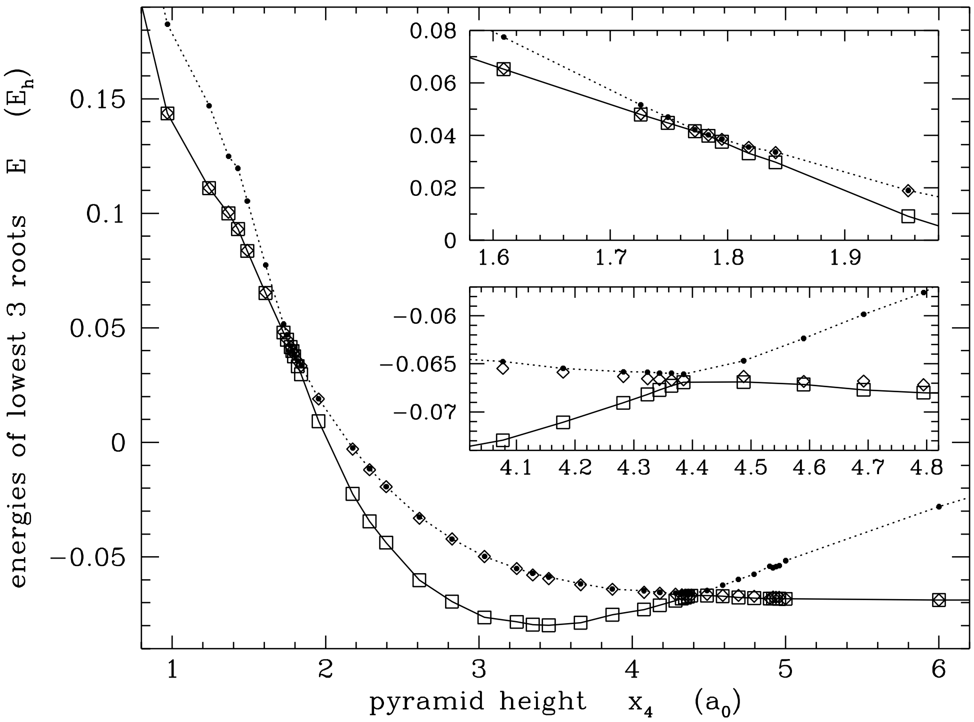

FIG. 1. The lowest three *ab initio* energies as a function of the pyramid height x_4, for an equilateral pyramid of base size $r_1 = 1.75\ a_0$. Squares (connected by solid line, to help guide the eye) indicate the ground state energy, diamonds the first excited state, and small filled circles (connected by dotted line, to help guide the eye) the second excited state. Insets show close-ups of regions around triply-degenerate "cross-over" points. Note that for these high-symmetry, relatively high-energy conformations a pair of degenerate roots may actually yield *ab initio* energies up to about 1 mE_h apart, due to the errors in the MRD-CI computation.

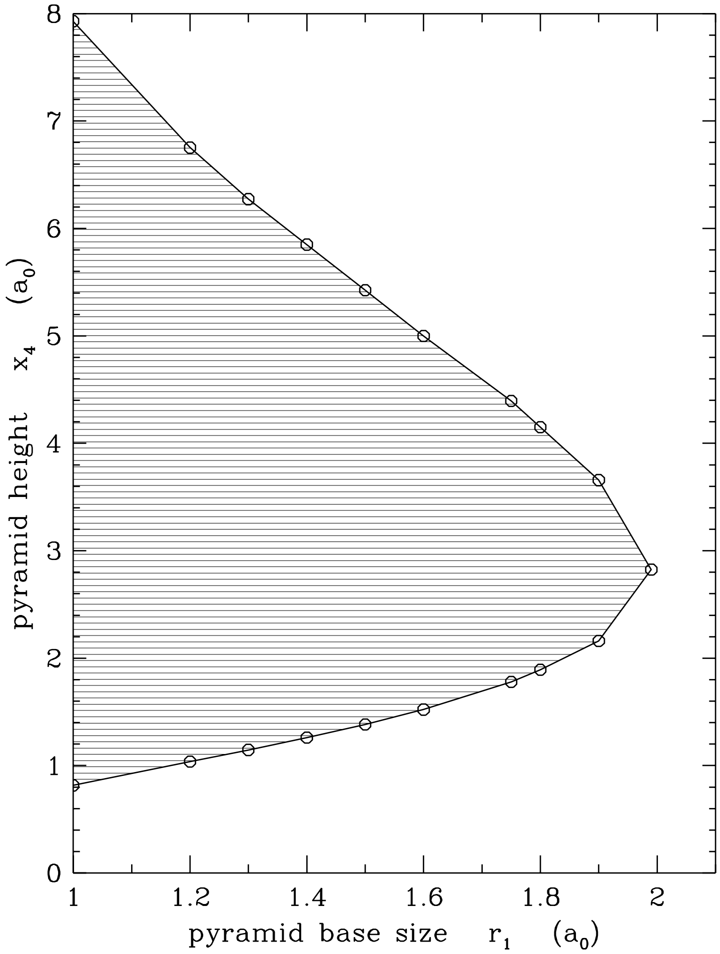

FIG. 2. For equilateral pyramids (C_{3v} symmetry) with base sides r_1 and height x_4 (with x_4 being the vertical distance above the center of the equilateral-triangle base), the shaded area indicates the region where the equilateral pyramids do *not* have a degenerate ground state energy (and thus do not lie on the conical intersection with the first excited state). The open circles (connected by the solid line) show the "switch-over" conformations where the ground state was found to be triply degenerate.

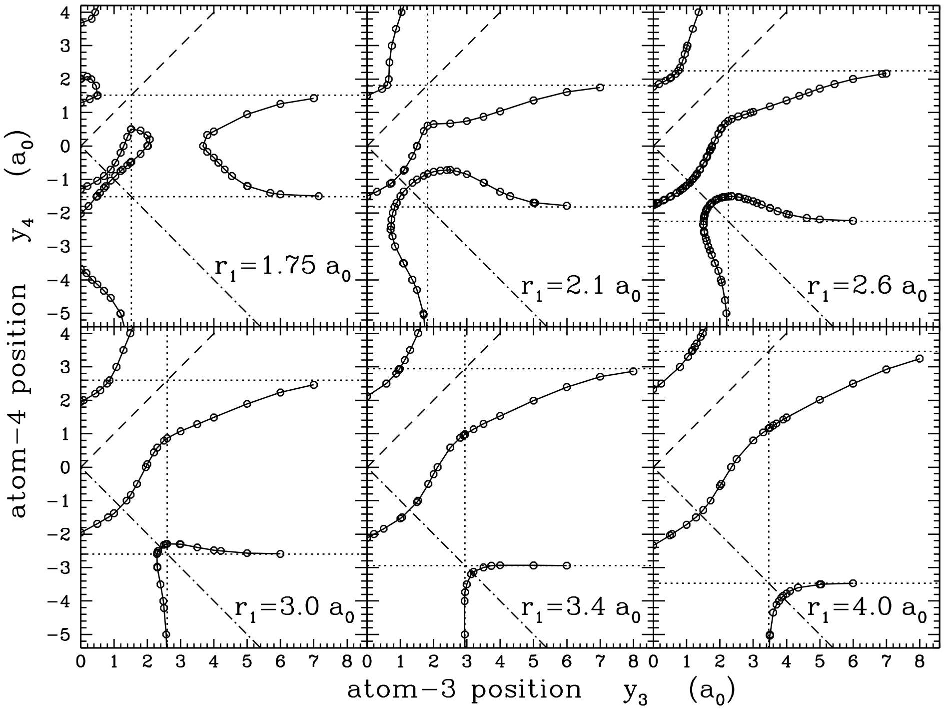

FIG. 3. Position of the conical intersection for planar conformations ($x_4 = 0$) at six values of r_1. Open circles (connected by solid lines) show the positions where *ab initio* computations indicate that the conical intersection occurs. Note that invariance under interchange of atoms 3 and 4 requires that there be reflection symmetry about the line $y_3 = y_4$ (dashed lines), and invariance under reflection in the x-z plane requires that there also be reflection symmetry about the lines $y_3 = -y_4$ (dot-dashed lines). Vertical (horizontal) dotted lines indicate positions where the third (fourth) atom makes an equilateral triangle with the first two atoms (which define r_1).

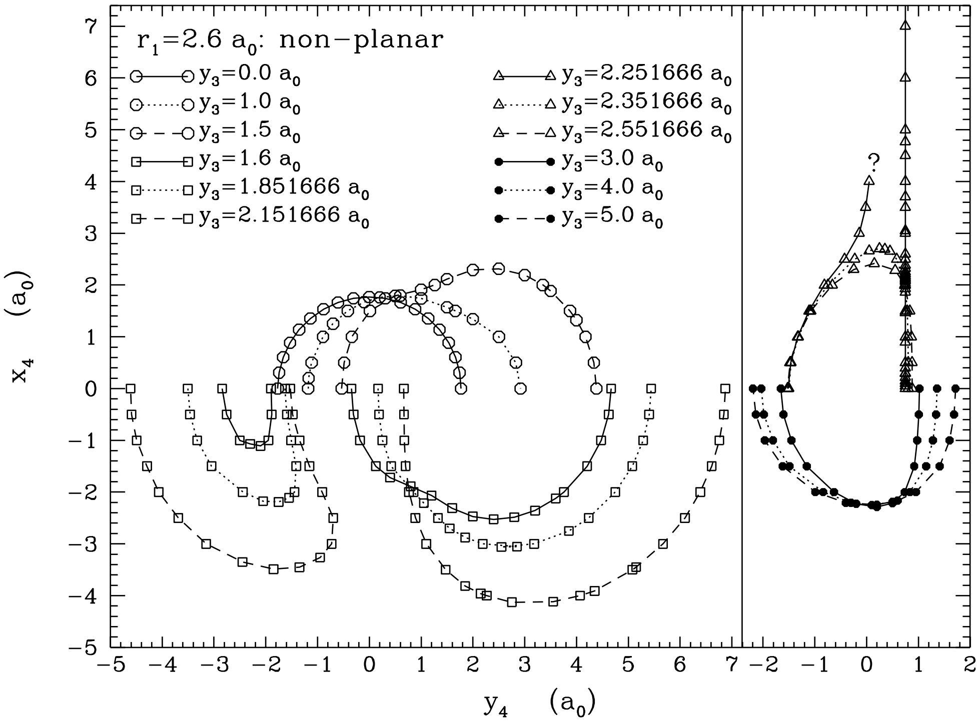

FIG. 4. Position of the conical intersection for non-planar conformations as a function of the position (x_4, y_4) of the fourth atom, for 12 positions y_3 of the third atom at $r_1 = 2.6\ a_0$. For clarity, the larger y_3 cases are shown in a separate panel at right; also, the position of the conical intersection is symmetric under reflection in the plane defined by the first three atoms, i.e., under $x_4 \to -x_4$, so only one sign of x_4 is plotted for any y_3 case. Note that for $y_3 = 2.251666\ a_0$ the first three atoms form an equilateral triangle.

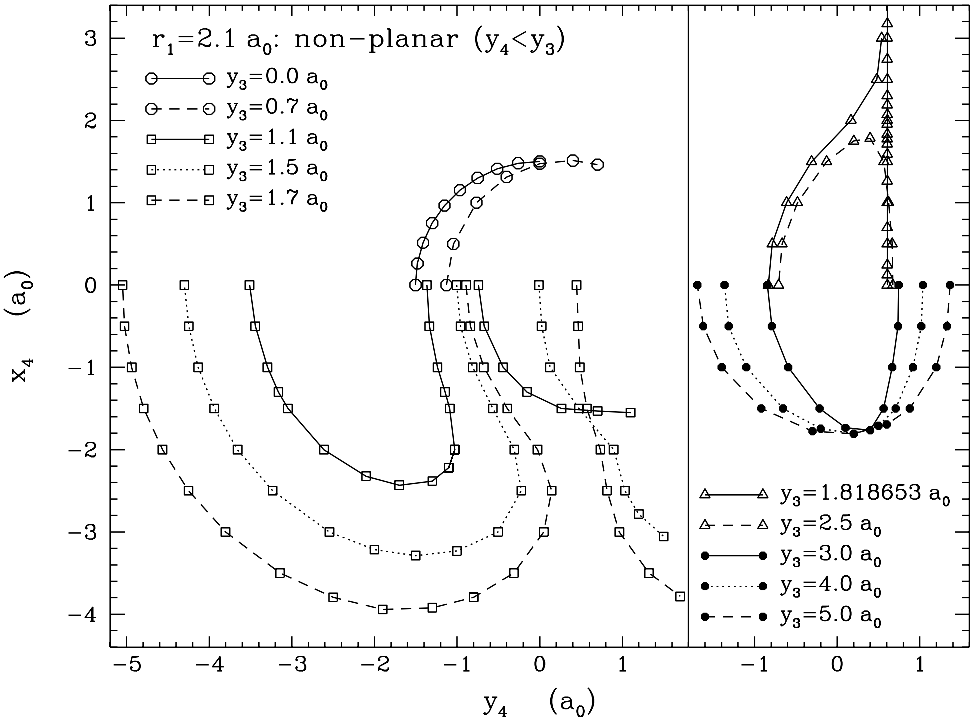

FIG. 5. Position of the conical intersection for non-planar conformations at a somewhat smaller value of $r_1 = 2.1\ a_0$; similar to Fig. 4, except that only cases with $y_4 < y_3$ are plotted. For $y_3 = 1.818653\ a_0$ the first three atoms form an equilateral triangle.

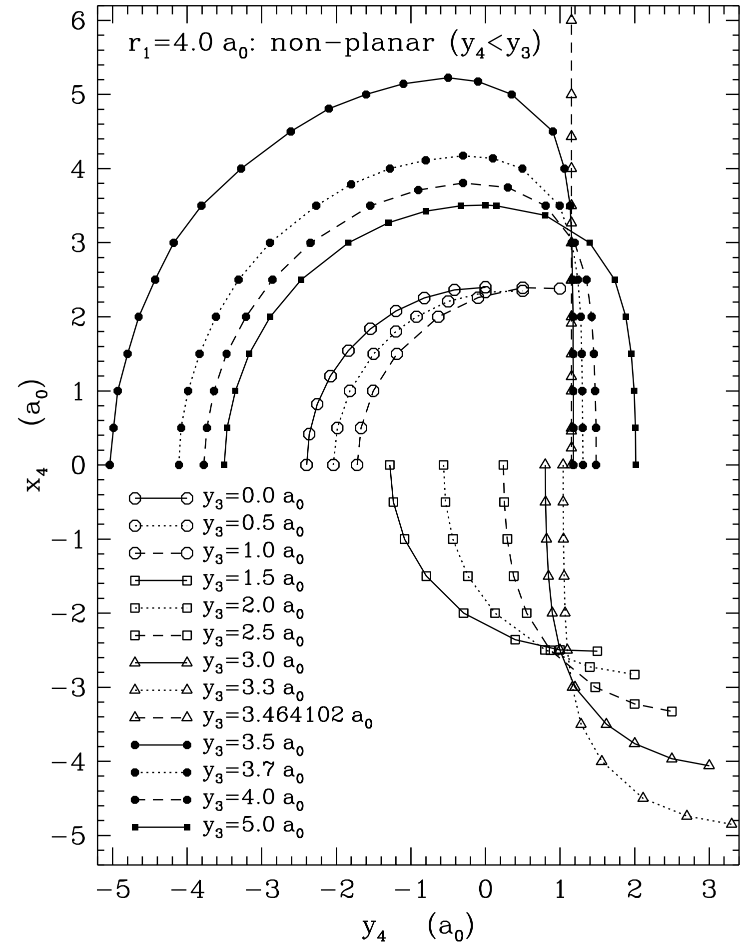

FIG. 6. Position of the conical intersection for non-planar conformations at a somewhat larger value of $r_1 = 4.0\ a_0$; similar to Fig. 5. For $y_3 = 3.464102\ a_0$ the first three atoms form an equilateral triangle.

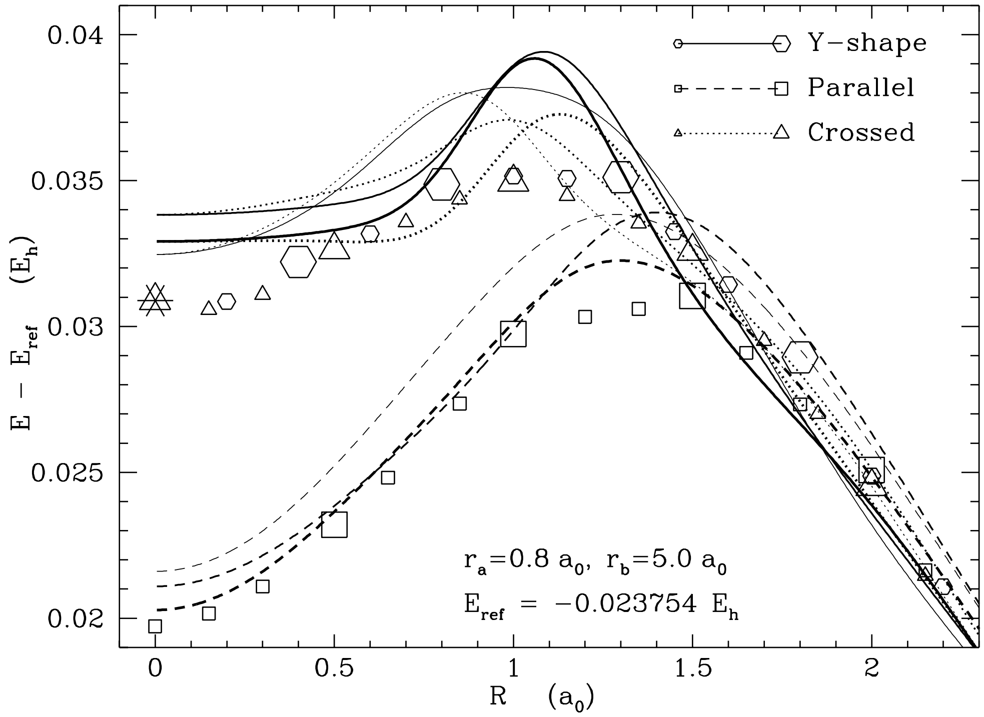

FIG. 7. An example where the adopted surface "Ad" does somewhat better than "A" or "G", for $r_a = 0.8\ a_0$ and $r_b = 5.0\ a_0$ (energy $E_{\rm ref}$ refers to $R \to \infty$). Discrete symbols indicate *ab initio* energies (double-sized symbols indicate fitted points; others are extra "test" points). Heavy curves show surface "Ad" (the adopted surface, with 400 parameters), medium curves show the corresponding 785-parameter surface "A", and light curves show the 791-parameter surface "G" (the best of the surfaces that had no London cusp-rounding). The "parallel" case refers to the case with $\vec{r}_a \parallel \vec{r}_b \perp \vec{R}$. The other three are cases with $\vec{r}_a \perp \vec{r}_b$, forming a "+" shape at $R = 0$; the "Y-shape" has $\vec{r}_a \parallel \vec{R}$, the "T-shape" (curve not shown) has $\vec{r}_b \parallel \vec{R}$, and the "crossed" case has $\vec{r}_a \perp \vec{R} \perp \vec{r}_b$.

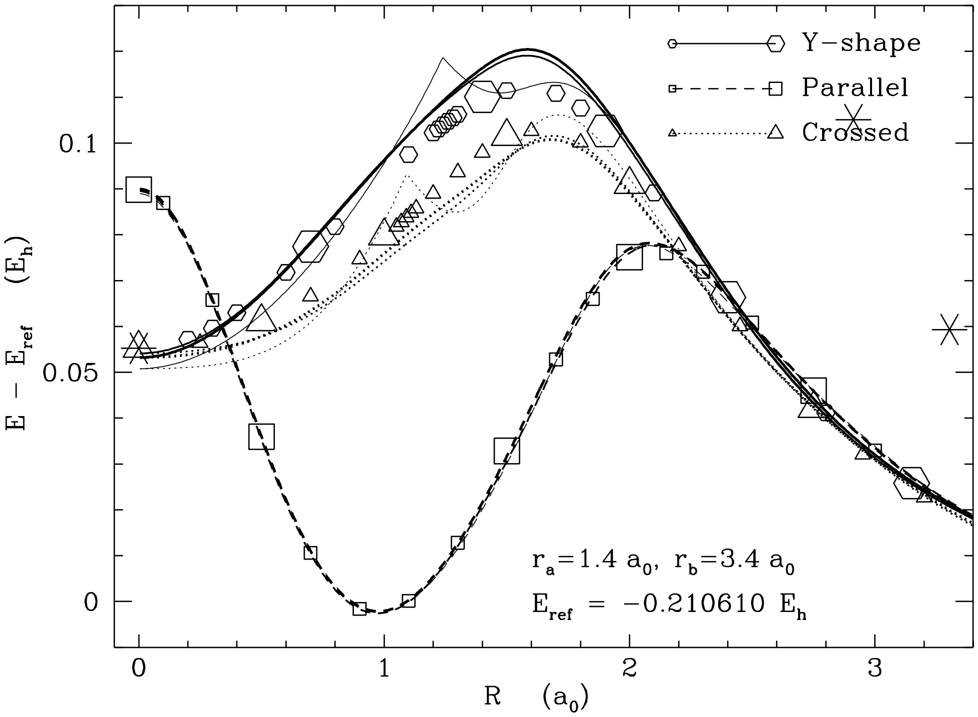

FIG. 8. An example where London cusp-rounding eliminates a spurious cusp of significant size from surface "G"; notation as in Fig. 7.

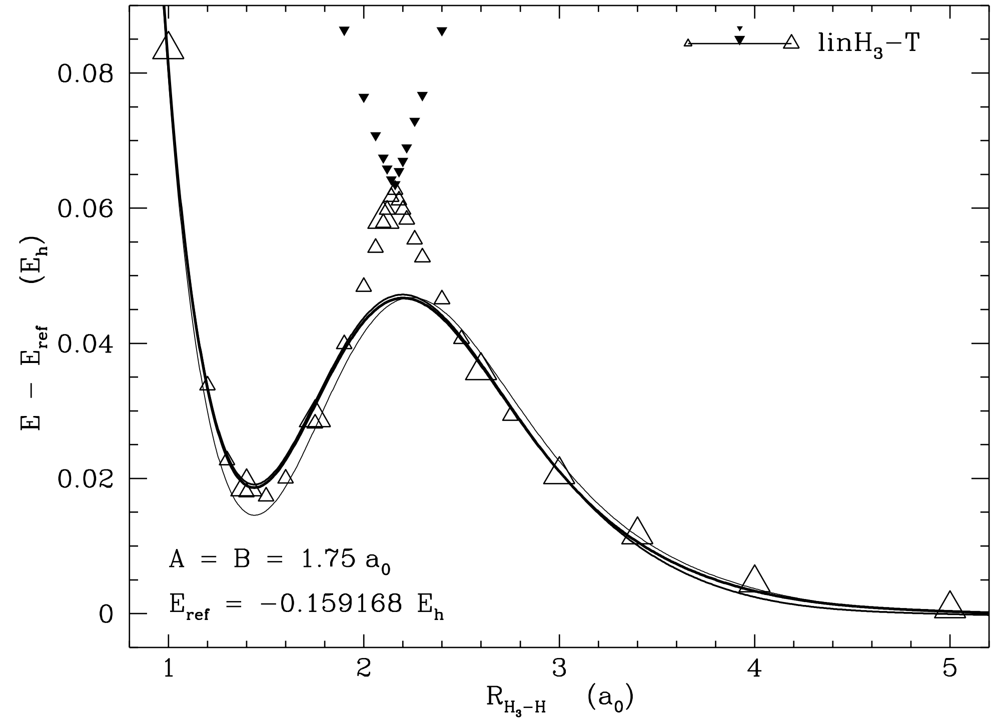

FIG. 9. An example where the conical intersection with the first excited state is approximated reasonably well by a "hill" in the fitted surface. For this "LinH$_3$-T" orientation, the distance R_{H_3-H} is that between a fourth H atom and the central atom of a linear-symmetric H$_3$ (that has interatomic separations $A = B = 1.75\ a_0$), with $\vec{A} \parallel \vec{B} \perp \vec{R}_{\mathrm{H_3-H}}$, forming a T-shape with respect to the linear H$_3$ (energy E_{ref} refers to $R_{\mathrm{H_3-H}} \to \infty$). Symbols for *ab initio* energies of the first and second excited states (in this case, larger and smaller solid triangles, respectively) are indicated immediately above the middle of the line-type legend (note that all second excited state energies lie offscale in this figure). As in previous figures, heavy curves show surface "Ad" (the adopted surface, with 400 parameters), medium curves show the corresponding 785-parameter surface "A", and light curves show the 791-parameter surface "G" (the best of the surfaces that had no London cusp-rounding).