Explicitly correlated potential energy surface of H_3^+, including relativistic and adiabatic corrections

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Introduction

H_3^+: three nuclei, two electrons

The simplest *polyatomic* molecule.

Unlike two-electron *atoms* and two-electron *diatomic* molecules (H_2), H_3^+ has resisted an accurate quantum mechanical for decades.

The PES (potential energy surface) of H_3^+ is now available with *submicrohartree accuracy* (error of about 0.1 μE_h or 0.02 cm^{-1}). (Cencek *et al.* 1998)

Highly sophisticated quantum chemical methods required Ansatz for the electronic wave function, that depends explicitly on the interelectronic distance r_{12}.

Two approaches:

(a) the R12-method (Kutzelnigg 1985, Kutzelnigg & Klopper 1991), a configuration-interaction (CI) method, augmented by terms linear in r_{12}.

(b) exponentially correlated Gaussians (or Gaussian geminals) (GG) (Rychlewski et $al.$ 1994) in which the basis consists of Gaussians depending on $\vec{r}_1$, $\vec{r}_2$ and $\vec{r}_{12}$.

Relativistic effects. Lowest order of perturbation theory (Kutzelnigg 1989) is sufficient.

Experimental information on H_3^+ is mainly in its infrared spectrum (Oka 1980, 2000). Challenge to reproduce and interpret the vibration-rotation term levels.

On the lowest nontrivial theoretical level (beyond the harmonic approximation) this requires the PES in a sufficiently large neighborhood of the equilibrium structure.

First step beyond the Born-Oppenheimer (BO) approximation: evaluation of the *adiabatic corrections*.

For full agreement between theory and experiment, and for unambiguous assignments, *non-adiabatic corrections* are necessary as well.

Hückel theory (HMO)

The Hückel matrices for H_3^+ in a cyclic (equilateral triangular) and an open (symmetric linear) structure

$$\begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix} \quad \begin{pmatrix} \alpha & \beta & 0 \\ \beta & \alpha & \beta \\ 0 & \beta & \alpha \end{pmatrix} \tag{1}$$

eigenvalues $(\alpha + 2\beta, \alpha - \beta, \alpha - \beta)$ and $(\alpha + \sqrt{2}\beta, \alpha, \alpha - \sqrt{2}\beta)$.

Table 1: HMO energies

molecule		E
H^+		0
H		α
H_2		$2\alpha + 2\beta$
H_2^+		$2\alpha + 2\beta$
H_3^+	cycl	$2\alpha + 4\beta$
H_3^+	lin	$2\alpha + 2\sqrt{2}\beta$
H_3^{+*}	cycl	$2\alpha + \beta$
H_3^{+*}	lin	$2\alpha + \sqrt{2}\beta$

Table 2: HMO binding energies

molecule		dissoc.	E(HMO)	E(exact)/$[E_h]$
H_2		2 H	2β	0.174
H_2^+		$H + H^+$	β	0.102
H_3^+	cycl	$H_2 + H^+$	2β	0.170
H_3^+	lin	$H_2 + H^+$	0.82β	0.105
H_3^{+*}	cycl	$H_2^+ + H$	0	-
H_3^{+*}	lin	$H_2^+ + H$	0.41β	0.013

Hückel theory predicts a binding energy 2β for H_3^+ w.r.t. $H_2 + H^+$, equal to that for H_2 w.r.t. 2 H, in good agreement with exact results.

Hückel theory also predicts a stable excited state of H_3^+ with the two lowest MOs each singly occupied, and with the energy minimum in the symmetric linear geometry.

Hückel theory does not distinguish between a singlet and a triplet state, but for the triplet only the stability with respect to the lowest *triplet dissociation limit* ($H_2^+ + H$) matters.

Table 3: HMO bond orders (p) vs. bond lengths (in a_0)

molecule		p	$r_{interpol}$	r_{exact}
H_2		1	1.4	1.40
H_2^+		0.5	2.0	2.00
H_3^+	cycl	0.667	1.70	1.65
H_3^+	lin	0.704	1.65	1.54
H_3^{+*}	cyl	-		
H_3^{+*}	lin	0.352	2.50	2.45

If we plot the bond length as function of the Coulson-Hückel bond order p, we can interpolate between H_2 and H_2^+ (and use that $r = \infty$ for $p = 0$). We get (in a_0 units)

$$r = a + b/p; \;\; a = 0.8; \;\; b = 0.6 \tag{2}$$

Inserting p, we can predict r for for the two structures of H_3^+.

Table 4: History (selective) of the accuracy for H_3^+

year	Ground state energy	method	author
1963	*-1.356*	DIM	Ellison
1965	-1.299	SCF	Preuss
1964	*-1.357*	dubious	Conroy (1969: *-1.347*)
1964	-1.333	CI	Christoffersen
1967	-1.336	PNO-CI	Kutzelnigg *et al.*
1967	-1.338	CI	Schwarz & Schaad
1970	-1.340	CI	Czismadia
1973	-1.343 4	GG	Salmon & Poshusta
1974	-1.339	CI	Carney & Porter
1986	-1.343 4	CI	Meyer *et al.*
1990	-1.343 822	GG	Alexander *et al.*
1992	-1.343 822	GG	Frye *et al.*
1992	-1.343 835	MC	Anderson
1993	-1.343 835	R12	Röhse *et al.*
1995	-1.343 835 62	GG	Cencek *et al.*

H_3^+ is the prototype of a 3-center-2-electron bond. This bond is about twice as strong as the corresponding 2-center-2-electron bond.

H_2 has a substantial *proton affinity* (418 kJ/mol) and must hence be classified as a *base*.

Compared to other *basic* molecules in the gas phase, e.g H_2O (160 kcal/mol= 670 kJ/mol) or ions, H_2 is an extremely weak base. By far much higher proton affinities than for isolated molecules are found for hydrogen-bonded *liquids*, such as water.

The study of the entire potential surface of H_3^+ in view of an understanding of the ro-vibrational spectrum started probably with Carney & Porter (1974).

An important step in advance was a paper by Meyer *et al.* (1986) It was based on traditional CI calculations (*not* including r_{12}-dependent terms).

Very elegant selection of the points of the PES to be computed, that was later followed by other authors (Röhse *et al.* 1994, Jaquet *et al.* 1998).

Meyer *et al.* have chosen 69 points of the PES, labeled by three integers n_a, n_x, and n_y, which are related to the Morse-type symmetry adapted deformation coordinates (MSADC) S_a, S_x, and S_y

$$S_a = 0.15n_a = (\tilde{R}_{12} + \tilde{R}_{13} + \tilde{R}_{23})/\sqrt{3} \tag{3}$$

$$S_x = 0.15n_x = (2\tilde{R}_{12} - \tilde{R}_{13} - \tilde{R}_{23})/\sqrt{6} = S_e \cos\phi \tag{4}$$

$$S_y = 0.15n_y = (\tilde{R}_{23} - \tilde{R}_{13})/\sqrt{2} = S_e \sin\phi, \tag{5}$$

with

$$\tilde{R}_{kl} = \frac{1}{\beta}\left\{1 - \exp\left[-\beta\left(\frac{R_{kl}}{R_{\mathrm{ref}}} - 1\right)\right]\right\}, \quad \beta = 1.3, \quad R_{\mathrm{ref}} = 1.65\ a_0. \tag{6}$$

These 69 points define a part of the whole PES from the minimum up to well above the barrier to linearity.

The functional form is chosen such that it can be used up to the asymptotic region (H^+ + H_2, H+H+H^+), but the most reliable part includes the energy-region up to $\approx$ 20000 cm^{-1} above the minimum.

The choice $\beta = 1.3$ in (6) is recommended for a region close to the minimum, while $\beta = 1.0$ has be used in the asymptotic region close to dissociation.

The essential progress in accuracy came with the use of explicitly correlated wave functions of the R12 and GG type, to be described now.

Monte-Carlo (MC) method is able to achieve microhartree accuracy for H_3^+. (Anderson 1992). Has not played a role for H_3^+.

The R12-method

Quantum chemical standard method to include electron correlation is configuration interaction (CI).

For two-electron system one can factor out the spin. For a singlet state the spinfree CI function is

$$\Psi = \sum_{p,q} c_{pq}\varphi_p(1)\varphi_q(2); \ \ c_{pq} = c_{qp} \tag{7}$$

this expansion converges slowly.

Actually, if L is the highest angular quantum number l of the φ_p included in the expansion (7), then the error goes as $(L+1)^{-3}$.

This is due to fact that the exact 2-electron wave function has a *correlation cusp* at the point of coalescence of two electrons (Kato 1957).

Figure 1: Schematic plot of the correlation cusp (Coulomb hole, upper curve), the Fermi hole (middle curve) and the hole for unnatural-parity singlet states (lower curve). The wavefunction is displayed as function of r_{12}.
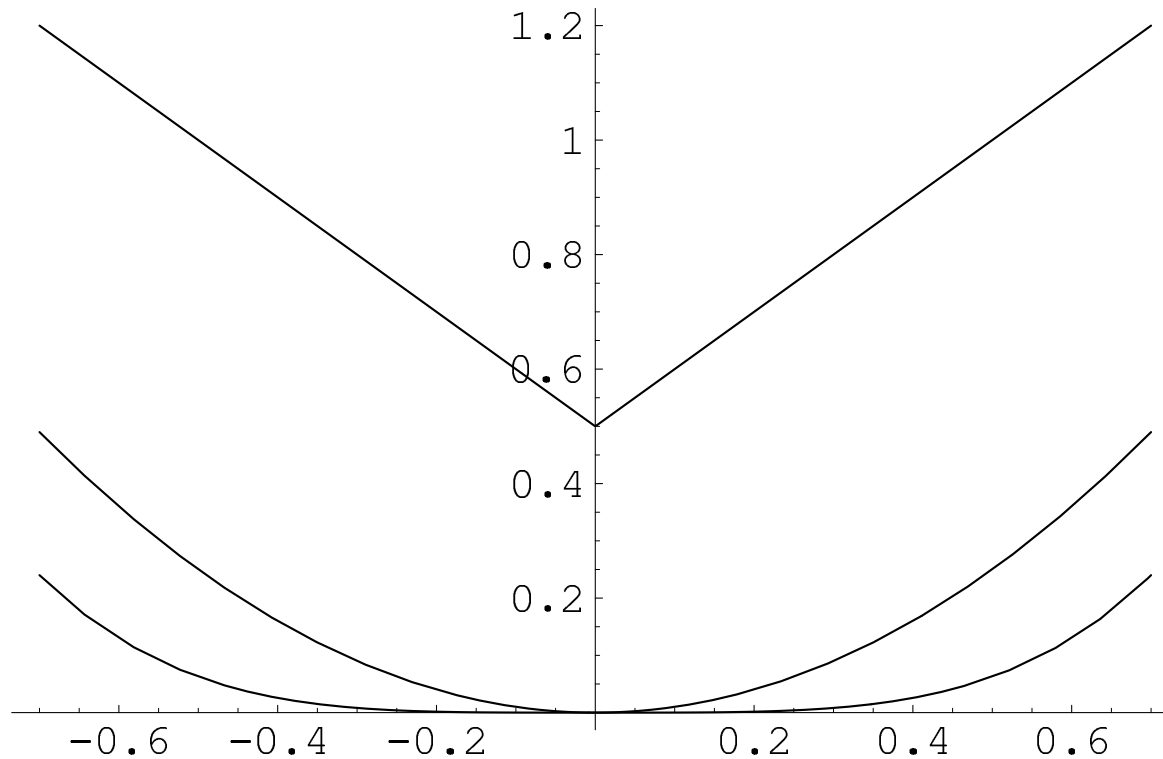
There the wave function is linear in r_{12}, which cannot be described by a CI wave function. A considerable speed-up of the convergence is obtained if one replaces (7) by

$$\Psi = c_0 r_{12}\Phi(1,2) + \sum_{pq} c_{pq}\phi_p(1)\phi_q(2); \; c_{pq} = c_{qp} \qquad (8)$$

where $\Phi(1,2)$ is a simple product-type *reference function*, e.g. an eigenfunction of the bare-nuclear Hamiltonian, i.e. the Hamiltonian for two non-interacting electrons in the field of two protons.

Table 5: Convergence of the l-expansion for H_3^+

Basis	conventional CI	CI-R12
30 s	-**1.3**11 981	-**1.3**34 632
30 s 20 p	-**1.34**1 332	-**1.343** 913
30 s 20 p 12 d	-**1.343** 338	-**1.343 835**
30 s 20 p 12 d 9 f	-**1.343** 656	-**1.343 835**

Now the error goes as $(L+1)^{-7}$.

The implementation of this ansatz requires in addition to the traditional electron repulsion integrals

$$\langle\phi_p(1)\phi_q(2)|\frac{1}{r_{12}}|\phi_r(1)\phi_s(2)\rangle \tag{9}$$

also the integrals (with T the operator of the kinetic energy)

$$\langle\phi_p(1)\phi_q(2)|r_{12}|\phi_r(1)\phi_s(2)\rangle; \ \ \langle\phi_p(1)\phi_q(2)|[T,r_{12}]|\phi_r(1)\phi_s(2)\rangle \tag{10}$$

With a (30s,20p,12d,9f) basis a ground state energy E $=$ -1.343835 E_h at the (equilateral triangular) equilibrium geometry has been obtained, with microhartree accuracy (Röhse $et\ al.$ 1994).

Omitting the f-functions in the basis, one gets errors of a few microhartrees. The size of the s, p, d is not so critical.

The published PES (Röhse $et\ al.$ 1994) was performed with a (16s10p8d) basis contracted to (10s8p6d), but for some points additional calculations with a contracted (10s8p6d4f) basis were performed.

More recent calculations on an extended region of the PES (Polyanski et al. 2000, Jaquet 2002) were done with the latter basis.

The method of exponentially correlated Gaussians

In the Gaussian geminal (GG) method (Rychlewski *et al.* 1994) for a 2-electron system in a singlet state one makes the following ansatz for the spinfree electronic wave function (Cencek *et al.* 1998):

$$\Psi \;=\; \sum_{i=1}^{K} c_i \phi_i \tag{11}$$

$$\phi_i \;=\; (1 + P_{12}) \exp(-\alpha_{1i}|\vec{r}_1 - A_i|^2 - \alpha_{2i}|\vec{r}_2 - B_i|^2 - \beta_i r_{12}^2) \tag{12}$$

All non-linear parameters α_{1i}, α_{2i}, and β_i, as well as the reference positions A_i and B_i are optimized consecutively in various cycles.

The optimization is stopped, when the gain in one cycle was less that 10^{-8} Hartree.

The expansion length was K=1300. Energy obtained at the equilibrium geometry E= -1.343835518 E_h was compared with the estimate for the exact value E= -1.343835624 E_h (Cencek *et al.* 1995), i.e. the error is of the order 0.1 microhartree or 0.02 cm^{-1}.

Unlike with the R12 method, one does, with Gaussian geminals, not describe the correlation cusp, i.e. the linear dependence of the wave function on r_{12} for $r_{12} \rightarrow 0$ correctly.

The excellent convergence is not immediately understandable.

Probably related to the satisfactory convergence of the expansion of one-electron-functions in a Gaussian basis (Kutzelnigg 1994).

Precursors of the refined application of the Gaussian geminal method were studies by (Salmon & Poshusta 1973, Alexander *et al.* 1990). Less sophisticated optimization of the non-linear parameters than later (Cencek *et al.* 1998).

Relativistic corrections

Relativistic corrections by means of direct perturbation theory (DPT) (Kutzelnigg 1989).

The result of DPT differs from that of the approximation (Bethe & Salpeter 1957) in a correction term Δ_{DPT} that takes care of a faster convergence of the overall result with extension of the basis, but which is not very important in the present case, since the non-linear parameters are well optimized.

The relativistic corrections involve expectation values of c^{-2} times the the following operators:

$$H_1 = -\frac{1}{2}(T_1^2 + T_2^2) \tag{13}$$

$$H_2 = -\frac{1}{2}\frac{1}{r_{12}}\left(\vec{p}_1\vec{p}_2 + \frac{\vec{r}_{12}(\vec{r}_{12}\vec{p}_1)\vec{p}_2}{r_{12}^2}\right) \tag{14}$$

$$H_4 = \frac{\pi}{2}\left(\sum_A Z_A[\delta(r_{1A}) + \delta(r_{2A})] - 2\delta(r_{12})\right) \tag{15}$$

$$H_5 = 2\pi\delta(r_{12}) \tag{16}$$

$$\Delta_{DPT} = \frac{1}{2}T(H_0 - E_0) \tag{17}$$

Adiabatic corrections

In the spirit of the Born-Oppenheimer approximation one first constructs a potential energy surface for clamped nuclei and one considers then the motion of the nuclei in this potential.

Not rigorous, nuclei have finite masses, which require corrections to the Born-Oppenheimer separation. Two types of corrections:

(a) the *adiabatic* or *diagonal* corrections, and

(b) the *non-adiabatic* or *non-diagonal* corrections.

Traditionally one first separates the center-of-mass motions (translation and rotation) from the relative motion and evaluates then the adiabatic corrections in terms of relative nuclear coordinates.

This leads to rather complicated expressions.

Handy *et al.* (1986, 1996) have proposed a much simpler approach, in which the center-of-mass motion is not separated off.

An *a-posteriori* justification is possible (Kutzelnigg 1997, see also Herman & Ashgarian 1966, Watson 1973)

The adiabatic correction E_{ad} is essentially the expectation value of the kinetic energy of the nuclei], evaluated with the electronic wave function (exploiting the parametric dependence of the latter on the nuclear coordinates).

$$E_{ad} = -\sum_{Q_i} \frac{1}{2M_i} \int \Psi \frac{\partial^2}{\partial Q_i^2} \Psi d\tau \tag{18}$$

It is a mass-dependent correction to the PES.

Table 6: Fundamentals for H_2D^+, in cm^{-1}

	BO	adiabat	exp
ν_1	2 993.75	2 992.38	2 992.49
$\frac{1}{2}(\nu_2 + \nu_3)$	2 270.72	2 270.68	2 270.66
$\nu_2 - \nu_3$	128.70	129.47	129.58

Table 7: Fundamentals for HD_2^+, in cm^{-1}

	BO	adiabat	exp
ν_1	2 737.84	2 736.87	2 736.98
$\frac{1}{2}(\nu_2 + \nu_3)$	2 023.44	2 023.26	2 023.30
$\nu_2 - \nu_3$	111.58	110.19	110.26

It has often been recommended to interpret the atomic energy unit (hartree) as a *reduced* unit, the equivalent of which in standard units (e.g. kJ/mol or cm^{-1}) depends on the nucleus (by choosing the reduced mass rather than the genuine electronic mass.

This choice makes only sense for atoms, and should not be used if one takes care of adiabatic corrections in the way indicated here (Kutzelnigg 1997). This would lead to a double-counting.

Non-adiabatic effects

For a correct evaluation of non-adiabatic effects one would have to consider the coupling of several electronic states.

Non-adiabatic effects cannot simply be taken care of by a correction to the PES.

For the H_2 molecule both the adiabatic and the non-adiabatic effects on the vibration frequencies are known rather accurately. The two effects are of comparable magnitude (Kolos *et al.* 1993).

Table 8: Adiabatic and non-adiabatic corrections to fundamental frequencies

	ν	adiabat.	non-ad.
H_2	4161.2 cm^{-1}	-1.4 cm^{-1}	-0.9 cm^{-1}
HD	3632.2 cm^{-1}	-1.0 cm^{-1}	-0.6 cm^{-1}
D_2	2993.6 cm^{-1}	-0.8 cm^{-1}	-0.3 cm^{-1}

Origin of the non-adiabatic correction to vibrational (rotational) frequencies is the partial participation of the electrons in the vibrational (rotational) motion. (Bunker & Moss 1977, Watson 1980, Moss 1996).

Simulate this effect by a change of the moving mass. For a full participation of the electrons one must – in neutral systems – replace the nuclear mass, that enters the Born-Oppenheimer approximation, by the atomic mass.

For H_3^+ : the mass of a proton plus two thirds of that of an electron.

Effective vibrational and rotational masses are different, the participation of the electrons in the rotation is more quenched than that in the vibration.

The non-adiabatic effects are of the order of a few tenths of a cm^{-1}, significantly smaller than for H_2.

Excellent agreement between theoretical and experimental term values (errors of a few hundredth to a few tenths of a cm^{-1}) if one uses the atomic mass for vibration, and the nuclear mass for rotation (Jaquet 1999).

In the region of avoided crossings the much larger *first-order* non-adiabatic effects must be considered.

Characterization of the H_3^+ ground state

Equilibrium geometry:
equilateral triangle (symmetry D_{3h}) r_e =1.6500 a$_0$ =0.8747 Å.

Binding energy
$D_e = 0.3438$ E$_h = 902.6$ kJ/mol $= 75\ 454$ cm^{-1} w.r.t. 2 H + H$^+$
$D_e = 0.1694$ E$_h = 444.8$ kJ/mol $= 37\ 178$ cm^{-1} w.r.t. H_2 + H$^+$.

Harmonic frequencies: 3 437.5 cm^{-1} (A_1); 2 775.0 cm^{-1} (E).

Lowest transitions: 3 178.3 cm^{-1} (A_1); 2 521.3 cm^{-1} (E).

Strong anharmonicity, nuclear motion by quantum mechanics.

Overtones and combination terms are classified by the occupation of ν_1 and ν_2, and an angular quantum number l_2.

19.87 mE_h = 4361.4 cm^{-1}. (H$_2$: 2180.2 cm^{-1}))

Rotational zero-point energy: 64.13 cm^{-1}

Dissociation energy: D$_0$=34 923.6 cm^{-1} w.r.t. H$_2$ + H$^+$.

Saddle point: symmetric linear structure $r_e = 1.5391a_0$

0.278682 E$_h$ = 731.693 kJ/mol = 61 162 cm^{-1} below 2 H+ H$^+$

22 886 cm^{-1} below H$_2$+ H$^+$

0.065151 E$_h$ = 171.057 kJ/mol = 14 299cm^{-1} above the D$_{3h}$ minimum.

Minimum energy path corresponds to dissociation into H$^+$ + H$_2$.

One cannot exclude the possibility of a dissociation into H + H$_2^+$.
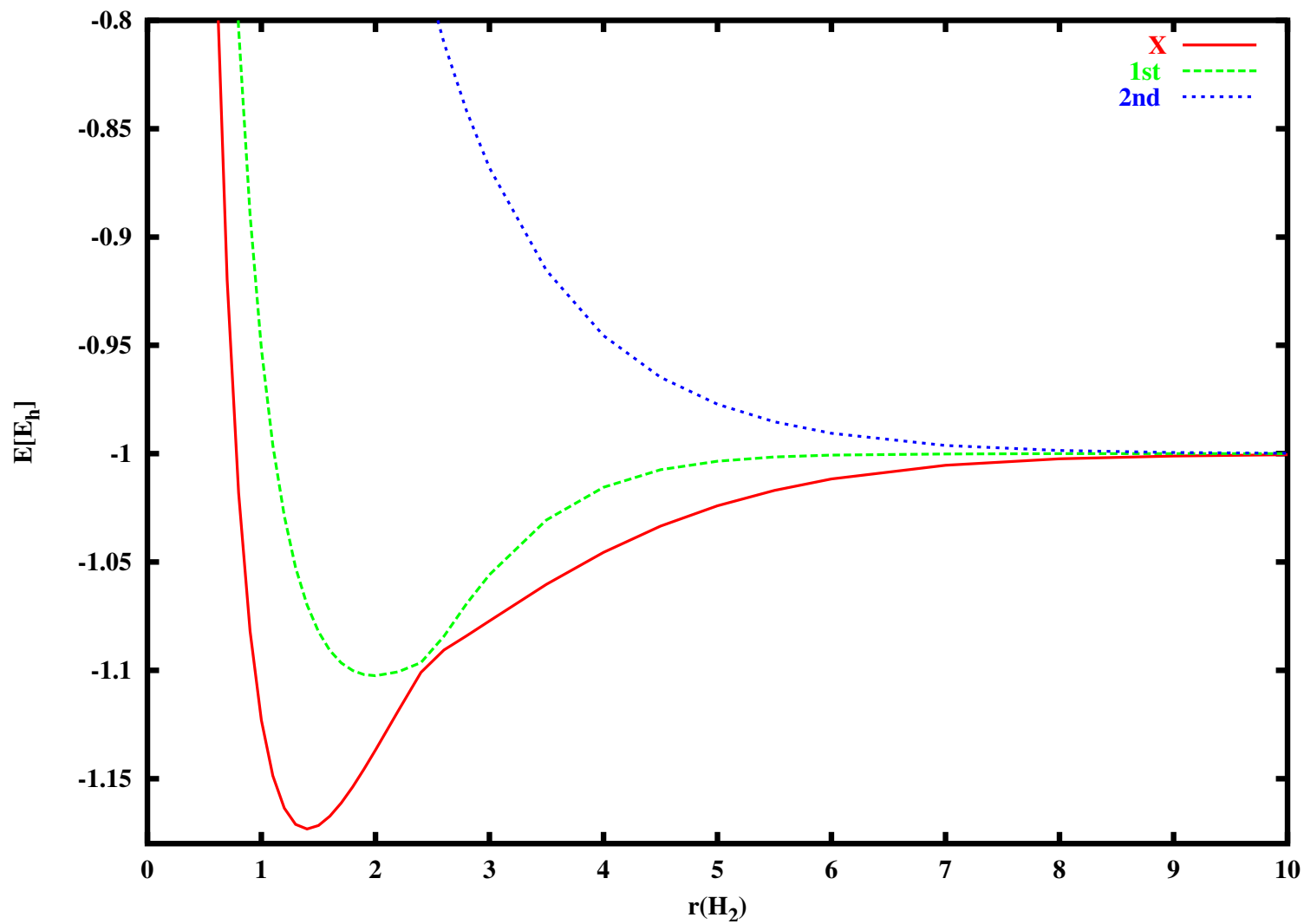
Figure 2: Cut through the PES of H_3^+ for $R \to \infty$

Crossing of the two curves at $r = 2.5017a_0$.

If one changes the Jacobi coordinate R (which measures the distance between H and H_2) from ∞ to finite values, the crossing becomes *avoided*.

The ground state of H_3^+ changes, near $r = 2.5a_0$, from the *diabatic* state characterized as $H^+ + H_2$ to the charge transfer type *diabatic* state characterized as $H + H_2^+$.

Close to this crossing extremely large adiabatic corrections (Jaquet 1999, 2002). A dynamic treatment requires to take care of both states.

Upper adiabatic state switches between the complementary diabatic states. See early DIM (diatomics in molecules) studies of H_3^+ (Tully & Preston 1971).
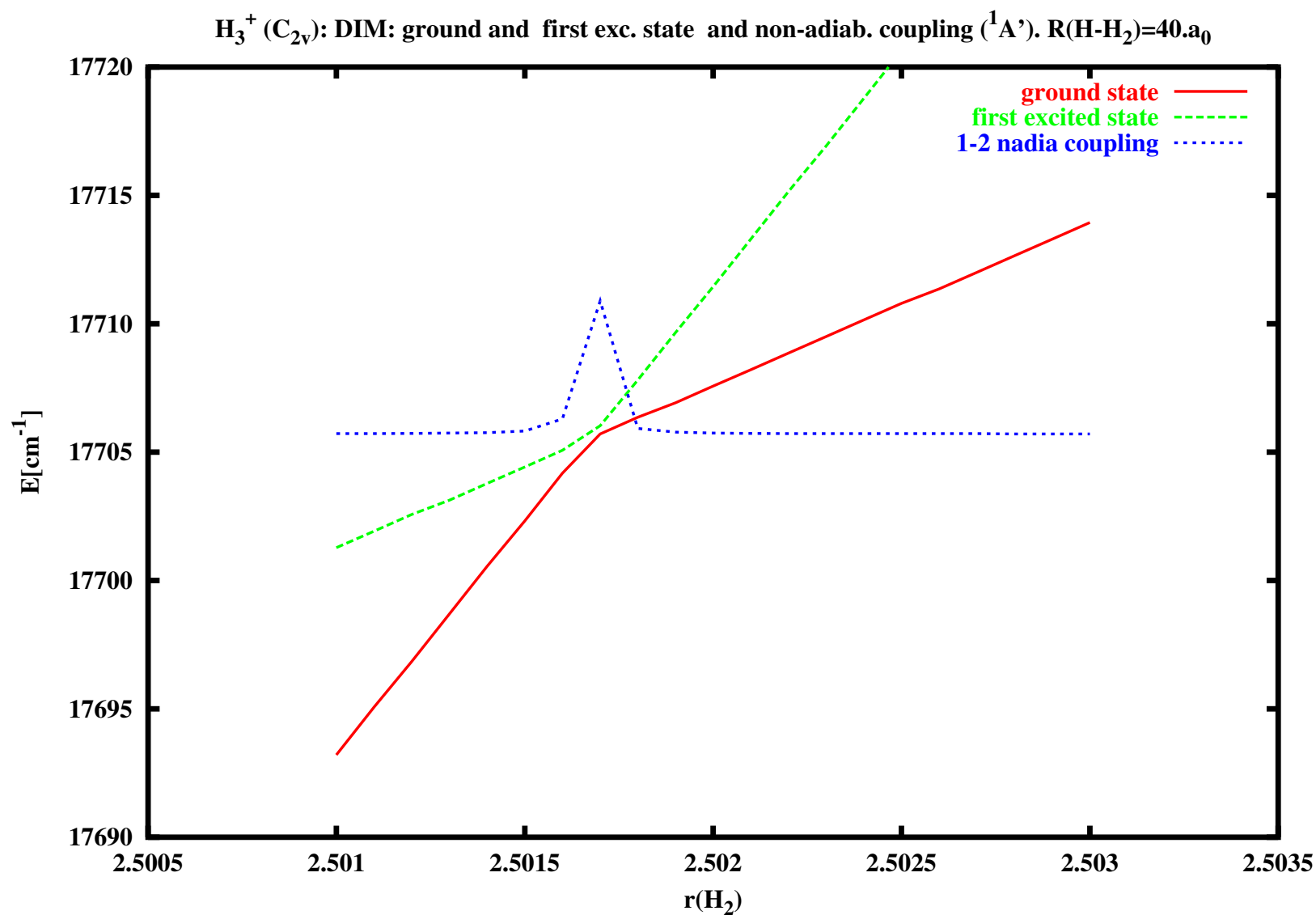
Figure 3: Non-adiabatic couplings in the region of the avoided crossing

Excited states of H_3^+

Schaad and Higgs (1974): H_3^+ has only two bound states, namely the singlet ground state and an excited triplet state. Even Hückel theory predicts a bound excited state of H_3^+ with linear equilibrium geometry.

See the lecture by Alijah on the bound triplet state of H_3^+.

Triplet less demanding from point of view of quantum chemistry.

Triplet wave functions vanish at the point of coalescence of two electrons. Cusp of higher order, error of a conventional partial wave expansion goes as $(L+1)^{-5}$ rather than as $(L+1)^{-3}$, as it does for singlet states.

CI without explicit inclusion of r_{12}-dependent terms usually sufficient.

In D_{3h} symmetry the triplet state has the configuration a_1e. As an E state it is degenerate and subject to a Jahn-Teller splitting, there are actually two PES which cross at D_{3h} symmetry, such that we have two PESs separated by a conical intersection.

The lower sheet has its minimum for symmetric linear geometry as predicted by Hückel theory, with $r = 2.4537a_0$ (Cernay *et al.* 2003).

This state dissociates into the lowest triplet asymptote H and H_2^+.

Binding energy: $D_e = 13.47\ mE_h = 2957$ cm^{-1} w.r.t. H + H_2^+.

C_{2v} saddle point 2.03 $mE_h = 446$ cm^{-1} below the asymptote, or 0.012 031 $E_h= 2600$ cm^{-1} above the minimum.

One expects a singlet counterpart of this triplet state. In regions where the subunits H and H_2^+ are far from each other, the exchange integral is small and the singlet state should only be slightly above the triplet state.

The excited singlet state should also have a Jahn-Teller splitting and a conical intersection.

Unpublished results (Jaquet): a shallow minimum, but no indication of a bound zero point vibrational level.

Avoided crossing with the ground state, near the dissociation asymptote.

Does H_3^+ have Rydberg states? This is related to the question whether there is a stable configuration of H_3^{2+} that can serve as the core for an outer electron.

Absolute minimum for H_3^{2+} probably a H_2^+ in its equilibrium and a proton at infinite distance. Rydberg states rather unlikely.

Analytic fit and accuracy of the potential energy surface

Analytic fit to the computed points of the potential surface is necessary.

Fit should be as accurate as are the computed points. It should interpolate smoothly, and not introduce spurious oscillations.

It should extrapolate reasonably to asymptotic regions.

Starting with Meyer *et al.* (1986) the Morse-type symmetry adapted deformation coordinates (MSADC) (3) to (5) became standard, namely as S_a, S_e, and ϕ. The energy is then expanded as a polynomial

$$V = \sum_{n,m,k} V_{n,m,k} S_a^n S_e^{m+k} cos(k\phi), \quad n + m + k \leq N_{max} \qquad (19)$$
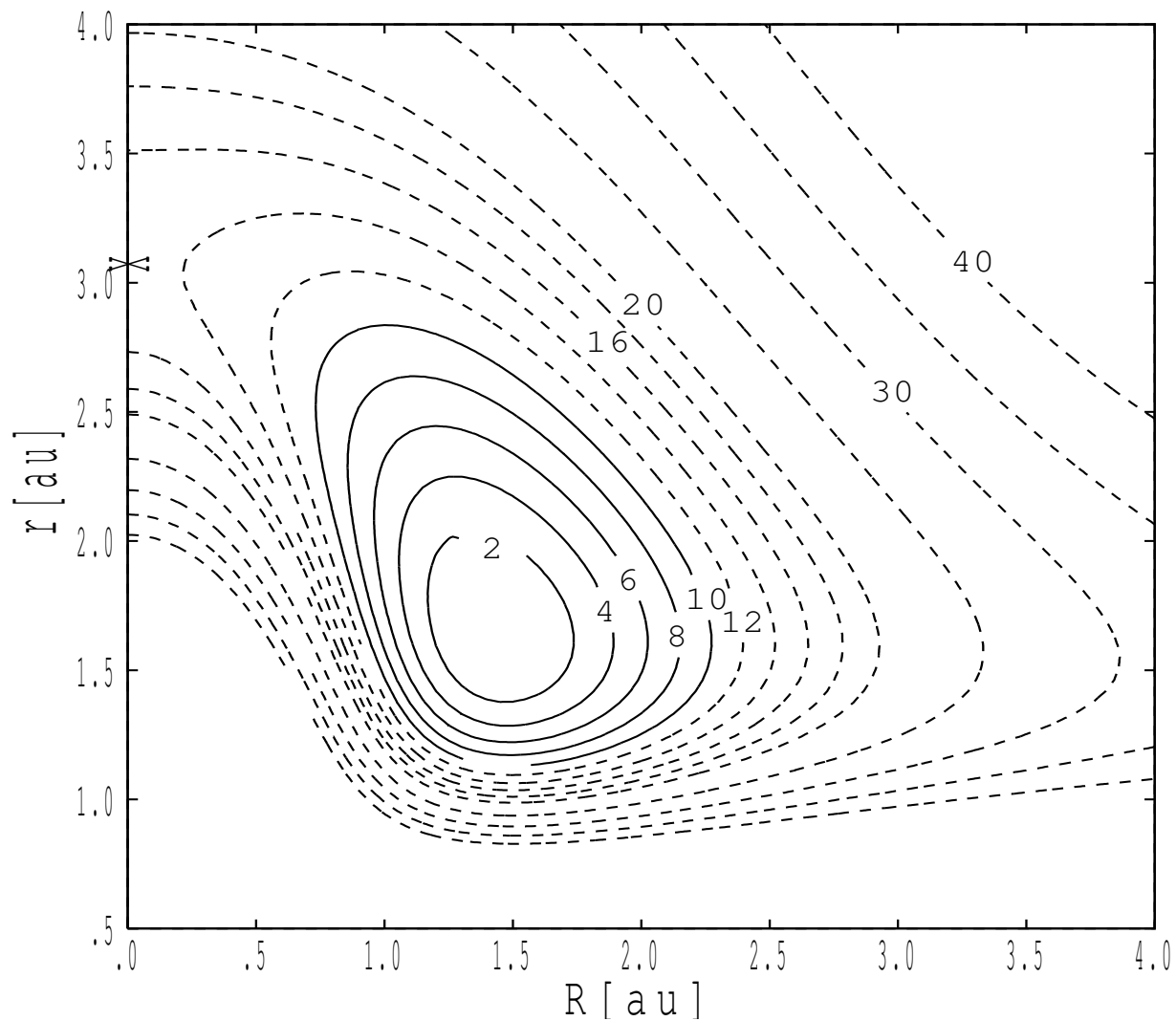
Figure 4: Plot of the PES of H_3^+ near the minimum in C_{2v}-symmetry, in terms of the Jacobi coordinates r and R in units of a_0. The linear saddle point is marked by X.
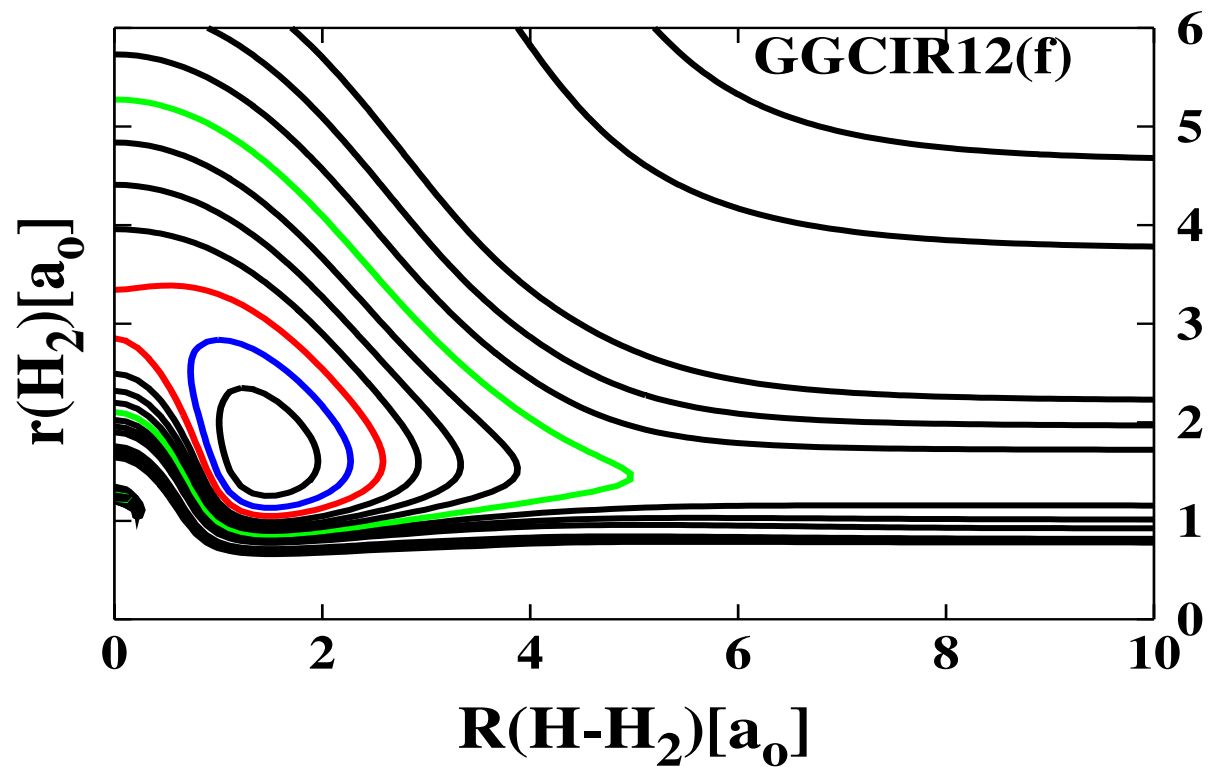
Figure 5: Plot of the PES of H_3^+ in C_{2v}-symmetry, in a larger range in terms of the Jacobi coordinates r and R in units of a_0.

Choice between a single fit for the total energy, and individual fits for the various contributions to the energy, that are then added up.

The separation of the fits has the advantage that the mass dependence of the adiabatic corrections is easily taken care of.

In the neighborhood of the minimum, the adiabatic corrections vary along the PES between 90 and 140 cm^{-1}, with a contribution of electron correlation to these corrections between 10 and 14 cm^{-1}, but they become very large for $R > 4a_0$.

Relativistic corrections negative and of the order of a few cm^{-1}.

Alternatives to standard polynomial fit: (a) the many-body expansion Varandas 1995) (b) the *reproducing kernel Hilbert space method* (RKHS), (Ho and Rabitz 1996), applied to the points computed by Röhse *et al.* (1994), (c) the Shepard interpolation (Collins 2002)

Table 9: Vibrational band origins of H_3^+ in cm^{-1}

symmetry	label	BO	adiabat	non-ad.	exp.
A_1	ν_1	3179.35	3178.68	3178.139	(3178.290)
	$\nu_2^2(0)$	4778.39	4778.75	4778.389	(4778.350)
E	ν_2	2521.59	2521.62	2521.416	2521.413
	$\nu_2^2(2)$	4998.40	4998.53	4998.130	4998.050
	$\nu_1\nu_2$	5555.49	5554.85	5554.151	(5554.155)
	$\nu_2^3(1)$	7006.22	7006.86	7006.344	(7006.187)
	$\nu_1\nu_2^2(2)$	7871.70	7871.05	7870.206	7870.016
A_2	$\nu_2^3(3)$	7493.86	7493.82	7493.210	7492.913

'BO' means calculations with nuclear masses on a BO surface

'adiabat' stands for calculations with nuclear masses on a surface with adiabatic corrections.

'non-ad.' means calculations with atomic masses (nucleus + 2/3 electrons) – to simulate non-adiabatic effects – on a surface with adiabatic corrections.

Experimental results from Lindsay & McCall, unpublished. Values in parentheses are not directly from the IR spectrum of H_3^+.

Shall one *improve* computed PSE by adjustable parameters to be fitted to experimental data (Dinelli *et al.* 1994)?.

It is usually possible to adjust even a poor surface, (provided it contains sufficiently many parameters) such that it reproduces all experimental data.

This may help to make predictions, but hardly leads to physical insight. For a meaningful empirical adjustment, two conditions must be satisfied:

(a) The error in the ro-vibrational spectrum must be a direct consequence of the inaccuracy of the surface, and e.g. not be due to non-adiabatic effects.

(b) All assignments in the observed spectrum must be beyond doubt.

To account for the low-lying IR frequencies (up to 8000 cm^{-1}) the 69 MBB points (Meyer et al. 1986) together with the polynomial fit (19) and the program TRIATOM (Tennyson & Sutcliffe 1984, Tennyson & Miller 1989) for the nuclear dynamics turned out to be sufficient.

The agreement between theoretical and experimental ro-vibronic frequencies is quite good (see table 9). This even holds for intensities, that have been evaluated recently (Jaquet 1999, 2003).
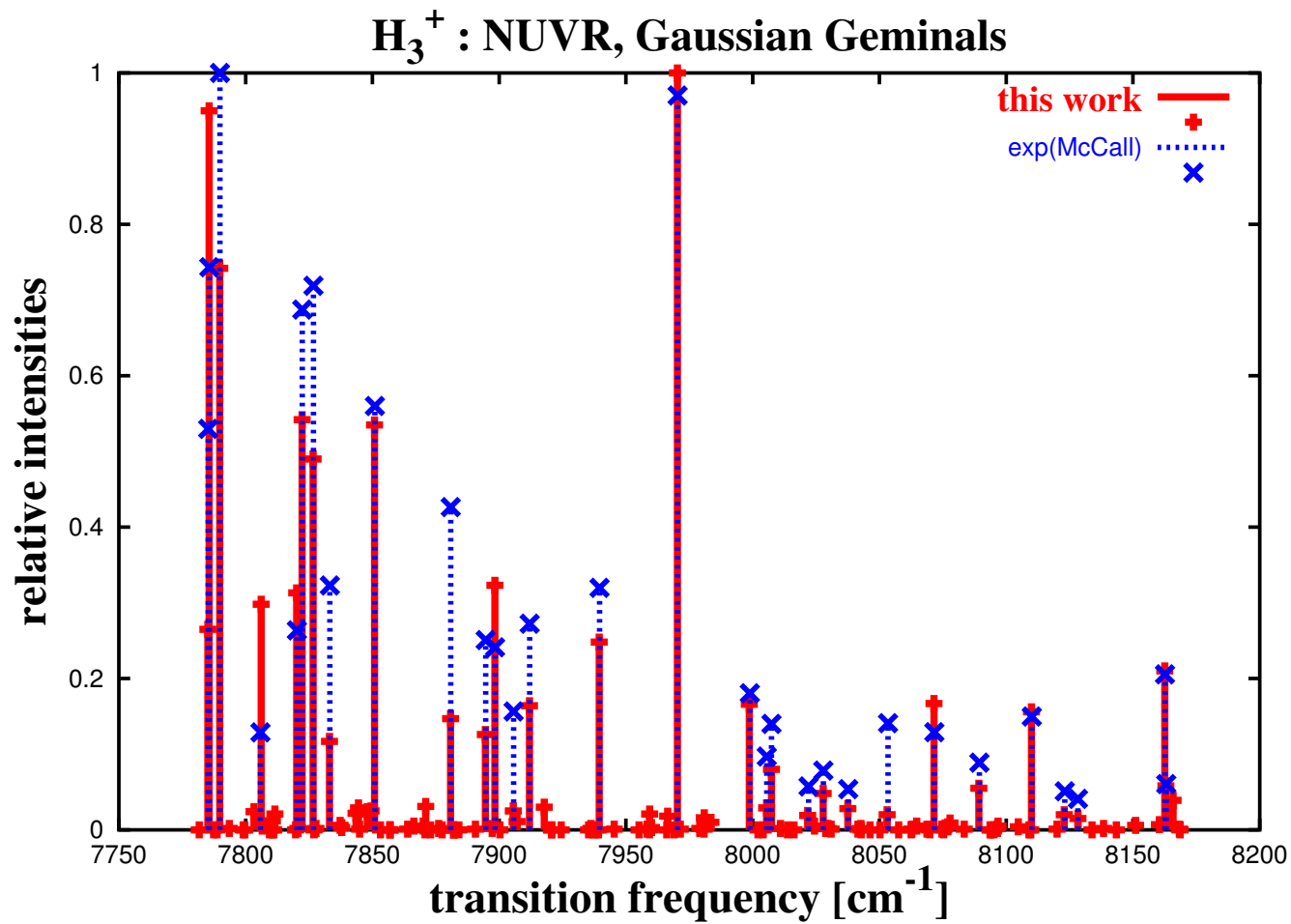
Figure 6: Comparison of computed and measured intensities

For the the spectrum in the higher frequency region many more points are necessary.

There appears further the need to test different fits and an alternative treatment of the nuclear dynamics, by means of e.g

DVR methods (Tennyson *et al.* 1993, Bramley *et al.* 1994),

hyperspherical coordinates (Alijah *et al.* 1995)

finite elements (Jaquet unpublished),

especially in the region close to and above the barrier to linearity.

Near the dissociation limit, one must consider the nuclear motion on the two singlet surfaces that have an avoided crossing for large R.
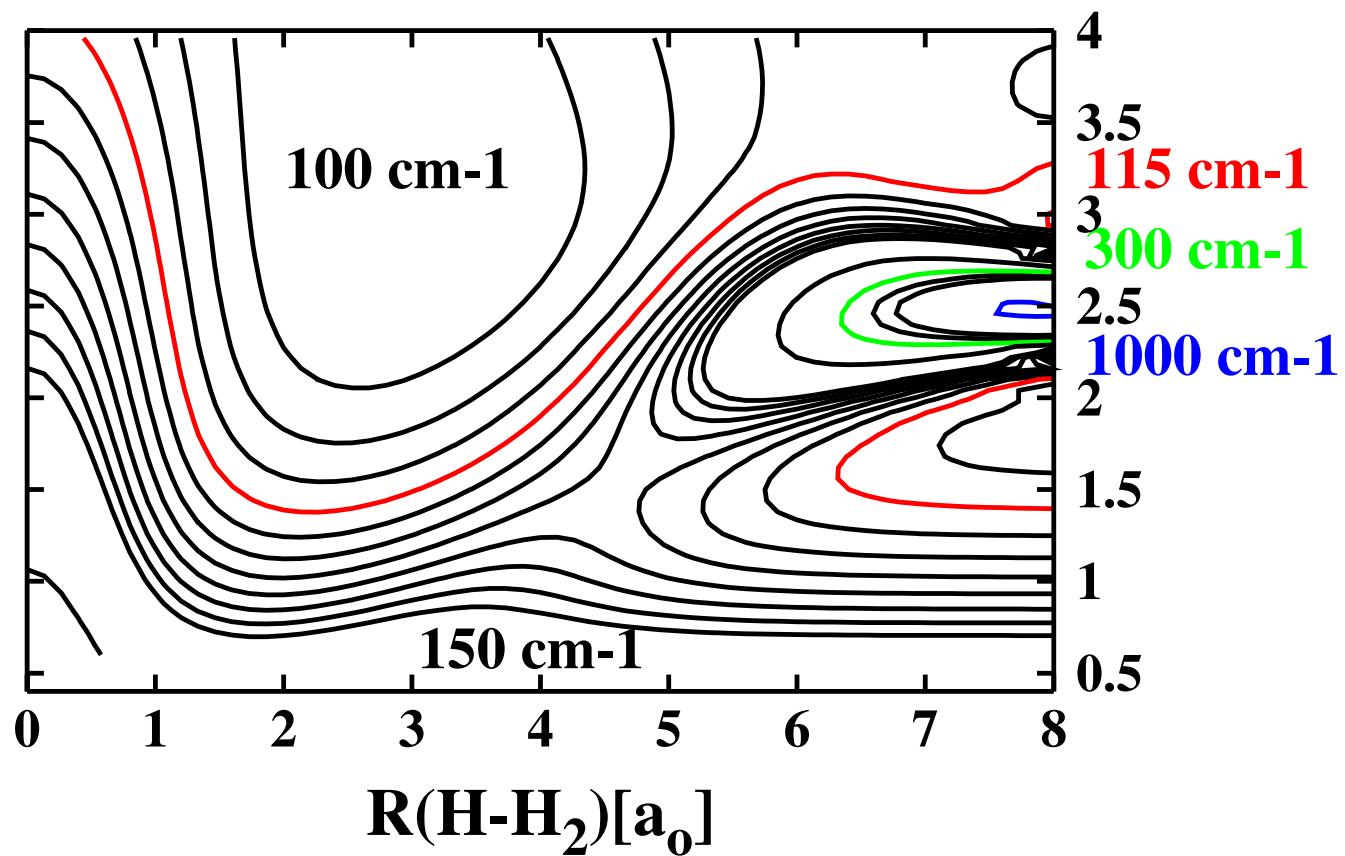
Figure 7: Adiabatic corrections in C_{2v} symmetry

A few words on H_5^+

Under the conditions under which H_3^+ is present, also addition complexes $H_3^+(H_2)_n$ are stable. Among these the ion H_5^+ plays a special role.

H_3^+ is the prototype of a 3-center-2-electron bond,

H_5^+ represents a 5-center-4-electron bond.

Bond between H^+ and H_2 particularly strong:
$D_e = 169 mE_h = 444 kJ/mol = 37091$ cm^{-1}.

Attachment of H_3^+ to H_2: $D_e = 13.7 \ mE_h = 35.9$ kJ/mol $= 3007$ cm^{-1}.

Although H_5^+ has only 4 electrons, it is from the point of view of Quantum Chemistry much harder than the 2-electron system H_3^+.

Both the R12 method and the Gaussian geminal method can be applied to H_5^+, but the accuracy that can be achieved, is much more modest than for H_3^+. So calculations with explicitly correlated wave functions were only performed for the most important stationary points of H_5^+ (Müller & Kutzelnigg 2000).

One of the reasons that limited the accuracy, is that 4-electron correlation effects, though small, are not entirely negligible.

We could afford CCSD(T)-R12 and CCSD[T]-R12 (which are hardly different) (Müller & Kutzelnigg 2000). CCSD-R12 is not sufficient.

Errors of the absolute energies of the order of 100 microhartree, but relative errors much smaller, 0.1 kJ/mol, i.e. significantly better than so-called chemical accuracy (Müller & Kutzelnigg 2000).
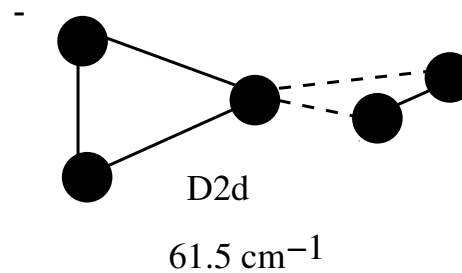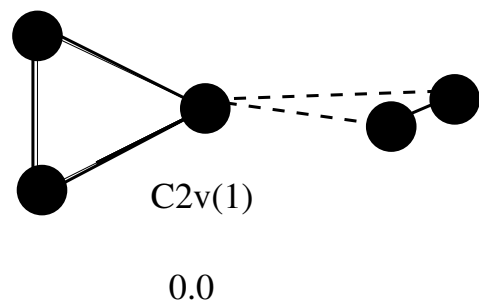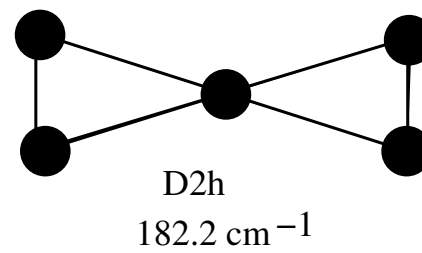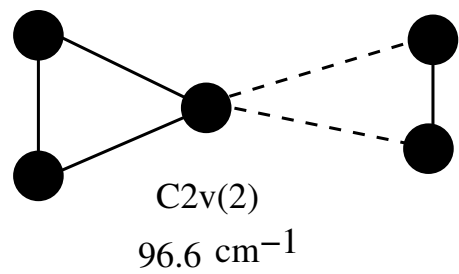
C2v(2)

96.6 cm^{-1}

D2h

182.2 cm^{-1}

C2v(1)

0.0

D2d

61.5 cm^{-1}

Figure 8: The lowest structures of H$_5^+$

Table 10: Distances and angles in H_5^+

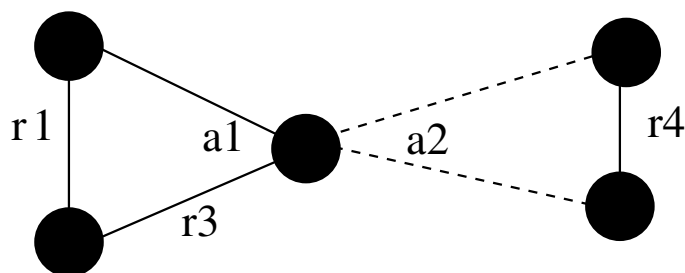|	r_1	r_3	α_1	r_4
$H_3^+ + H_2$	0.873	0.873	60°	0.741
H_5^+, C_{2v}	0.816	0.966	50°	0.765
H_5^+, D_{2d}, D_{2h}	0.780	1.125	41°	0.780
$H_2 + H^+ + H_2$	0.741			0.741

Figure 9: Geometrical parameters of H_5^+

Hartree-Fock: H_5^+ a rather loose complex between H_3^+ and H_2.

Electron correlation strongly stabilizes symmetric structures (Ahlrichs 1975). In low level of correlation treatment (IEPA) D_{2d} is lowest.

10 stationary points of the H_5^+ PES (Yamaguchi *et al.* 1987), 4 of these are very close in energy (within less than 200 cm^{-1}). The other 6 are higher by 1500 to 3000 cm^{-1}.

The structures $C_{2v}(1)$ and $C_{2v}(2)$ have practically the same geometrical parameters for the subunits H_3^+ and H_2 and also the same distance between them, they only differ in the twist angle. Similarly the structures D_{2d} and D_{2h} differ significantly only in the twist angle.

Taking care of the change in the zero-pont energy, beyond the harmonic approximation (Kraemer & Spirko 1994) using a double-well potential for H_5^+, we get D_0 for H_5^+ w.r.t. H_3^+ + H_2 of 25.5 kJ/mol= 2132 cm^{-1}, and for D_5^+ of 28.4 kJ/mol = 2374 cm^{-1}.

Recent Monte Carlo result for the zero-point energy (Xie *et al.* 2005): 6.33 kcal/mol = 26.5 kJ/mol = 2215 cm^{-1} for H_5^+.

The dynamics of H_5^+ has been studied by Kraemer *et al.* (1993) and Spirko *et al.* (1994), and more recently by Xie *et al.* (2005).

H_5^+ is a very floppy molecule, all protons are easily scrambled. The Longuet-Higgins group (1963) has the order 240 (like that of CH_5^+).

The harmonic vibrational frequencies have been evaluated for the $C_{2v}(1)$ structure (Prosmiti *et al.* 2001). The two lowest frequencies are 202 and 506 cm^{-1}. Their zero-point levels lie high above the 3 next stationary points.

The 4 lowest stationary points have no physical reality. The vibrational ground state is highly symmetric, with practically free internal rotation.

One must further consider that along the path through a double well the zero point energy of the vibrations perpendicular to this path change, which manifests itself as a change of the effective potential for isomerization.

References

[1] Ahlrichs, R. 1975 *Theor. Chim. Acta.* **39**, 149.

[2] Alexander, S. A., Monkhorst, H. J. & Roeland, R., Szalewicz, K. 1990 *J. Chem. Phys.* **93**, 4230.

[3] Alijah, A. in this issue

[4] Alijah, A., Hinze, J. & Wolniewicz, L. 1995 *Mol. Phys.* **85**, 1105, 1125.

[5] Anderson, J. B. 1992 *J. Chem. Phys.* **96**, 307.

[6] Bethe, H. A. & Salpeter, E. E. 1957 *Quantum Mechanics of One- and Two-electron atoms*. Berlin: Springer.

[7] Bukowski, R. Jeziorski, B. & Szalewicz, K. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 158-248.

[8] Carney, G. D. & Porter, R. N. 1974 *J. Chem. Phys.* **60**, 4251; 1976 **65**, 3547.

[9] Cencek, W., Komasa, J. & Rychlewski, J. 1995 *Chem. Phys. Lett.* **246**, 417.

[10] Cencek, W. & Kutzelnigg, W. 1997 *Chem. Phys. Lett.* **266**, 383.

[11] Cencek, W., Rychlewski, J. , Jaquet, R. & Kutzelnigg, W. 1998 *J. Chem. Phys.* **108**, 2831.

[12] Cencek, W. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 347-372.

[13] Christoffersen, R. E. 1964 *J. Chem. Phys.* **41**, 960.

[14] Czismadia I. G., Kari, R. E., Polanyi J. C., Roach A. C. & Robb M. A. 1970 *J. Chem. Phys.* **118**, 2637.

[15] Coulson, C. A. 1935 *Proc. Camb. Phil. Soc.* **31**, 244.

[16] Coulson, C. A. 1938 *Proc. Camb. Phil. Soc.* **34**, 204.

[17] Dinelli, B. M., Miller, S. & Tennyson, J. P. 1994 *J. Mol. Spectrosc.* **163** 71.

[18] Gottfried, J. L., McCall, B. J. &Oka, T. 2003 *J. Chem. Phys.* **118** 10890.

[19] Handy, N. C., Yamaguchi, Y. & Schaefer III, H. F. 1986 *J. Chem. Phys.* **84**, 4481.

[20] Handy N. C.& Lee, A. M. 1986 *Chem. Phys. Lett.* **252**, 425.

[21] Herman, R. M. & Asgharian, A. 1966 *J. Mol. Spectr.* **19**, 305.

[22] Hirschfelder, J. O., Eyring, H., Rosen, N. 1936 *J. Chem. Phys.* **4**, 130.

[23] Hirschfelder, J. O., 1936 *J. Chem. Phys.* **6**, 795.

[24] Ho, T. S. & H. Rabitz, H. 1996 *J. Chem. Phys.* **104**, 2584.

[25] Hückel, E. *Z. Phys.* **70**, 204; 1932 **76**, 628.

[26] Hylleraas, E. A. 1929 *Z. Phys.* **54**, 347.

[27] James, H. M. & Coolidge, H. M. 1933 *J. Chem. Phys.* **1**, 825.

[28] Jaquet, R., Cencek, W., Kutzelnigg, W. & Rychlewski, J. 1998 *J. Chem. Phys.* **108**, 2837.

[29] Jaquet, R. 1999 *Chem. Phys. Lett.* **302**, 27.

[30] Jaquet, R. 2002 *Spectrochimica Acta A***58**, 691.

[31] Jaquet, R. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 503-544.

[32] Kato, T. 1957 *Comm. pure appl. math.* **10**, 151.

[33] Klopper, W. & Noga, W. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 149-180.

[34] Kraemer, W. P., Spirko, V. & Bludski, O. 1994 *J. Mol. Spectr.* **164**, 500.

[35] Kutzelnigg, W. , Ahlrichs, R., Labib-Iskander, I. & Bingel, W. A. 1967 *Chem. Phys. Lett.* **1**, 447.

[36] Kutzelnigg, W. 1978, 1994, 2002 *Einführung in die Theoretische Chemie, Band 2, Die Chemische Bindung*. Weinheim: Wiley VCh.

[37] Kutzelnigg, W. 1985 *Theor. Chim. Acta.* **68**, 445.

[38] Kutzelnigg, W. 1989 *Z. Phys.* **11**, 15.

[39] Kutzelnigg, W. & Klopper, W. 1991 *J. Chem. Phys.* **94**, 1985.

[40] Kutzelnigg, W. 1994 *Int. J. Quant. Chem.* **51**, 447

[41] Kutzelnigg, W. 1996 *Phys. Rev.* **A54**, 1183.

[42] Kutzelnigg, W. 1997 *Mol. Phys.* **90**, 909.

[43] Kutzelnigg, W. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 3-90.

[44] Longuet-Higgins, H. C. 1963 *Mol. Phys.* **6**, 445.

[45] Meyer, W., Botschwina, P. & Burton, P. G. 1986 *J. Chem. Phys.* **84**, 891.

[46] Moss, R. E. 1996 *Mol. Phys.* **89**, 195. ; Bunker, P. R. & Moss, R. E. 1997 *Mol. Phys.* **33**, 417.

[47] Moyano, G. E. & Collins, M. A. 2003 *J. Chem. Phys.* **119**, 5510.

[48] Müller, H. & Kutzelnigg, W. 2000 *Phys. Chem. Chem. Phys.* **2**, 2061.

[49] Oka, T. 1980 *Phys. Rev. Lett.* **45**, 531.

[50] Oka, T. 2000 *Phil. Trans. R. Soc. Lond. A***358**, 2363.

[51] Polyansky, O. L., Prosmiti, R., Klopper, W. & Tennyson, J. 2000 *Mol. Phys.* **98**, 261.

[52] Porter, R. N. 1982 *Ber. Bunsenges. Phys. Chem.* **86**, 407.

[53] Prosmiti, R., Buchachenko, A. A., Villarreal, P. & Delgado-Barrio, G. 2001 *Theor. Chim. Acta.* **106**, 426.

[54] Röhse, R. & Gdanitz, R. .... .

[55] Röhse, R., Klopper, W. & Kutzelnigg, W. 1993 *J. Chem. Phys.* **99**, 8830.

[56] Röhse, R., Kutzelnigg, W. , Jaquet, R. & Klopper, W. 1994 *J. Chem. Phys.* **101**, 2231.

[57] Rychlewski, J. & Cencek, W. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 249-274.

[58] Rychlewski, J., Cencek, W. & Komasa, J. 1999, *Chem. Phys. Lett.* **229**, 657.

[59] Rychlewski, J. & Komasa, J. 2003, in *Explicitly Correlated Wave Functions in Chemistry and Physics*, J. Rychlewski, ed., Kluver, Dordrecht , p. 503-544.

[60] Salmon, L. & Poshusta, R. D. 1973 *J. Chem. Phys.* **59**, 3497.

[61] Schaad, L. J. & Hicks, W. V. 1974 *J. Chem. Phys.* **61**, 1934.

[62] Schwartz M. E. & Schaad, L. J. 1967 *J. Chem. Phys.* **47**, 5325.

[63] Spirko, V., Kraemer, W. P. & Soldan, P. 1997 *J. Mol. Spectr.* **183**, 218.

[64] Sutcliffe, B. T. Sutcliffe, B. T. & Tennyson, J. 1991 *Int. J. Quant. Chem.* **29**, 183.

[65] Tennyson, J., & Sutcliffe, B. T. 1984 *Mol. Phys.* **51**, 887.

[66] Tennyson, J., & Miller, B. T. 1989 *Comput. Phys. Commun.* **55**, 149.

[67] Tully, J. & Preston,

[68] Varandas A. C. J., Alijah, A. & Cernay. M. & 2005 *Chem. Phys.* **308**, 285.

[69] Watson, J. K. G. 1973 *J. Mol. Spectr.* **45**, 99.

[70] Watson, J. K. G. 1980 *J. Mol. Spectr.* **80**, 411.

[71] Watson, J. K. G. 1984 *J. Mol. Spectr.* **103**, 350.

[72] Watson, J. K. G. 2000 *Phil. Trans. R. Soc. Lond. A***358**, 2371.

[73] Yamaguchi, Y., Gaw, J. F., Remington R. B., Schaefer, H. J. III, 1987 *J. Chem. Phys.* **86**, 5072.

[74] Xie, X., Braams, B. J. & Bowman, J. E. 2005 *J. Chem. Phys.* **122**, 224307.

[75]