

Studies of reaction dynamics and spectroscopy of hydrocarbons in plasma

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Our project

Potential energy surfaces

MULTIMODE

Sample applications

Outlook

Our project

Funded by USDOE, Fusion Energy Science, started 2007.

Rate coefficients for reactions of H and H₂ on CH_n, C₂H_n, C₃H_n; neutral or once charged.

Rovibrational spectra of CH_n⁺, C₂H_n⁺, C₃H_n⁺.

Tools: Potential energy surface fitting; quasiclassical trajectory calculations; MULTIMODE spectroscopy.

Main challenge: Electronic excited states, surface hopping.

Potential energy surfaces

Born-Oppenheimer approach: $V = V(X)$

X : Collective nuclear coordinates.

$V(X)$: Total energy; from solution of electronic Schrödinger equation.

PES V then used for molecular dynamics or quantum mechanics.

Also dipole moment surface (DMS) $\mathbf{d}(X)$, a vector quantity.

Sample Bowman Group applications

- ▶ CH_5 , CH_5^+ , H_5^+
- ▶ H_3O_2^- , H_4O_2 , H_5O_2^+
- ▶ C_3H_2 , $\text{C}_3\text{H}_3\text{O}$
- ▶ C_2H_3^+ , C_2H_5^+ (Amit Sharma, Ralf Schneider)
- ▶ HONO_2 , HOONO
- ▶ CH_3OH , CH_3CHO , CHOHCHCHO

Choice of coordinates

Considerations

- ▶ V is invariant under translation, rotation, reflection. Thus, $3N - 6$ independent coordinates.
- ▶ V is invariant under permutations of like nuclei.

Use functions of the internuclear distances, $r(i,j) = \|\mathbf{x}(i) - \mathbf{x}(j)\|$. For example, let $y(i,j) = \exp(-r(i,j)/\lambda)$; hence vector $y \in \mathbf{R}^d$, $d = N(N - 1)/2$; and then $V = p(y)$.

Polynomial p must be invariant under permutations of like nuclei.

Important earlier work: [J. N. Murrell et al., *Molecular Potential Energy Functions*, Wiley, 1984]. 3- and 4-atom systems.

Permutation symmetry group

Say N nuclei, indexed by $\{i : 1 \leq i \leq N\}$.

Say K different kinds; hence partition $N = n_1 + \dots + n_K$.

\Rightarrow Group $G = \text{Sym}(n_1) \times \dots \times \text{Sym}(n_K)$.

Non-standard representation. Variables $y \in \mathbf{R}^d$ ($d = N(N-1)/2$); components $y(i, j)$ ($i \neq j$); $y(i, j) = y(j, i)$. Permutation $\pi \in G$:

$$\pi : (\pi y)(i, j) = y(\pi^{-1}i, \pi^{-1}j)$$

Need polynomials of $y \in \mathbf{R}^d$ invariant under $\text{Sym}(n_1) \times \dots \times \text{Sym}(n_K)$ acting on \mathbf{R}^d .

Dipole moment also requires covariants $\mathbf{R}^d \rightarrow \mathbf{R}^N$.

\Rightarrow Invariant theory of finite groups.

Invariants of finite groups - Introduction

Easy case: Polynomials on \mathbf{R}^n invariant under $\text{Sym}(n)$.

Generated by the elementary monomials:

$$p_k(x) = \sum_i x_i^k$$

Every invariant polynomial $f(x)$ has a *unique* representation in the form $f(x) = \text{poly}(p_1(x), \dots, p_n(x))$.

[Computational cost $O(1)$ per term; compare with $O(n!)$ per term for symmetrized monomial basis.]

Just as easy: Polynomials on $\mathbf{R}^{n_1+\dots+n_K}$ invariant under $\text{Sym}(n_1) \times \dots \times \text{Sym}(n_K)$ in the “natural” representation.

Invariants of finite groups - General

Not easy: $\text{Sym}(n_1) \times \cdots \times \text{Sym}(n_K)$ in our not so natural representation on \mathbf{R}^d , $d = N(N-1)/2$.

Theory for the general case: invariant polynomials for a finite group G acting on a finite dimensional vector space (say \mathbf{R}^n): [Harm Derksen and Gregor Kemper, *Computational Invariant Theory*, Springer Verlag, 2002].

There exists a family of n *primary generators*, invariant polynomials p_i ($1 \leq i \leq n$), together with a family of *secondary generators*, invariant polynomials q_α , such that every invariant polynomial $f(x)$ has a *unique* representation in the form

$$f(x) = \sum_{\alpha} \text{poly}_{\alpha}(p_1(x), \dots, p_n(x)) q_{\alpha}(x).$$

Invariants of finite groups - Example

Illustration: Case of $G = \text{Sym}(2)$ acting on \mathbf{R}^2 generated by inversions: $(x, y) \mapsto (-x, -y)$. May choose $p_1(x, y) = x^2$, $p_2(x, y) = y^2$, and $q_1(x, y) = 1$, $q_2(x, y) = xy$. Then:

$$f(x, y) = \text{poly}_1(x^2, y^2) + \text{poly}_2(x^2, y^2)xy$$

Example for a molecular group, the X₅Y₂ molecule.

$G = \text{Sym}(5) \times \text{Sym}(2)$ acting on \mathbf{R}^{21} (21 internuclear distances). We have 21 primary invariants: 3 of degree 1, 5 of degree 2, 3 of degree 3, 4 of degree 4, 3 of degree 5, 2 of degree 6 and 1 of degree 10. The number of secondary invariants at degrees 0..9 is 1, 0, 1, 12, 39, 113, 338, 932, 2402, 5678.

MAGMA computer algebra system

Developed at the University of Sydney, and elsewhere.

Includes representation theory of finite groups.

- ▶ W. Bosma and J. Cannon: The Magma Handbook, Eight Volumes, 3100 pages.
- ▶ Gregor Kemper and Allan Steel (1997) *Some Algorithms in Invariant Theory of Finite Groups*.

Use MAGMA to obtain primary and secondary invariants.

Convert MAGMA output to Fortran code.

Done for all molecular symmetry groups for at most 7 atoms.

Many-body expansion

Example for H_3C_2 complex:

$$V_{\text{all}} = V_{\text{H}} + V_{\text{C}} + V_{\text{H}_2} + V_{\text{HC}} + V_{\text{C}_2} + V_{\text{H}_3} \\ + V_{\text{H}_2\text{C}} + V_{\text{HC}_2} + V_{\text{H}_3\text{C}} + V_{\text{H}_2\text{C}_2} + V_{\text{H}_3\text{C}_2}$$

in which, for example

$$V_{\text{H}_2\text{C}} = \sum_{\substack{i,j \in \text{"H"} \\ i < j}} \sum_{k \in \text{"C"}} f_{\text{H}_2\text{C}}(r_{ij}, r_{ik}, r_{jk})$$

and then $f(x) = p(y(x)) \text{damp}(x)$ and, component-wise, for example, $y(x) = \exp(-x/\lambda)$

Coefficients of each such p from weighted least squares.

Numerical example

Example, X5Y2 (H_5O_2^+ , H_5C_2 , H_5C_2^+); single expansion.

$N = 7$, $d = 21$ ($N(N - 1)/2$); polynomials up to degree 7.

Using symmetry, approximation space has dimension 8,717.

Without using symmetry, dimension $\binom{28}{7}$, = 1,184,040.

Least squares system: ~ 50000 equations in ~ 8717 unknowns.

Can do larger problems using single expansion; 8-atom systems with sufficient symmetry. Beyond that, always use many-body expansion.

MULTIMODE

Normal coordinates Q_k . Hartree basis from harmonic oscillator functions ϕ_m .

$$\Phi_n(Q) = \prod_{k=1}^{3N-6} \phi_{n_k}(Q_k)$$

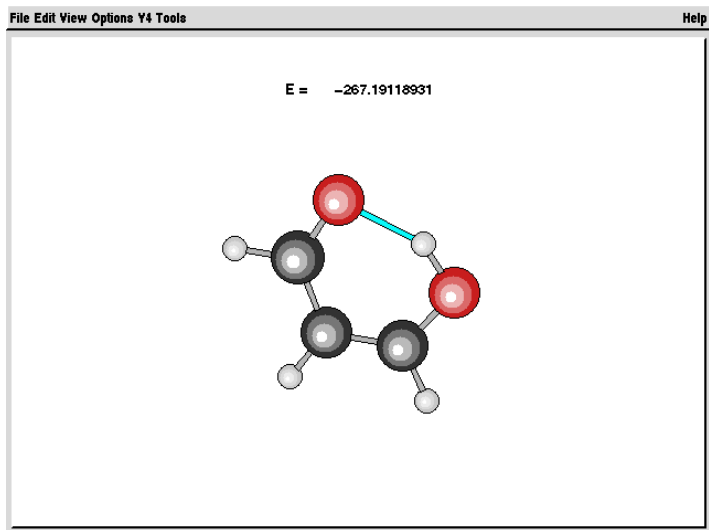
Expansion of the wavefunction:

$$\Psi_\nu = \sum_n C_n^\nu \Phi_n(Q)$$

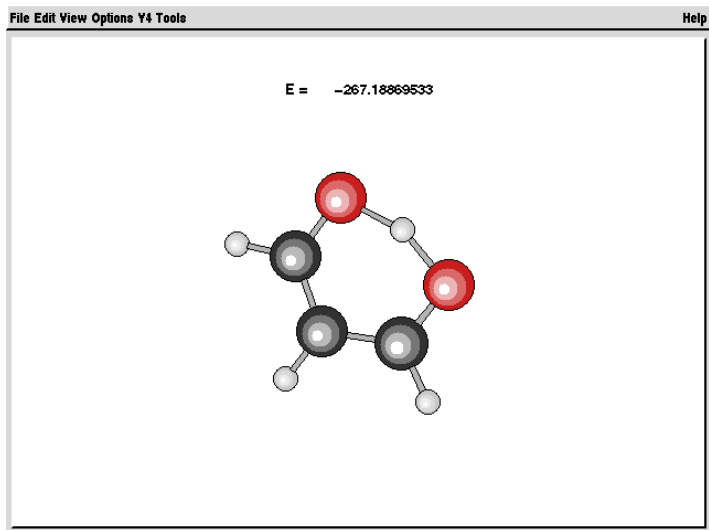
Expansion of the potential:

$$V(Q) = V^{(0)} + \sum_k V_k^{(1)}(Q_k) + \sum_{k,l} V_{k,l}^{(2)}(Q_k, Q_l) + \sum_{k,l,m} V_{k,l,m}^{(3)}(Q_k, Q_l, Q_m) + \dots$$

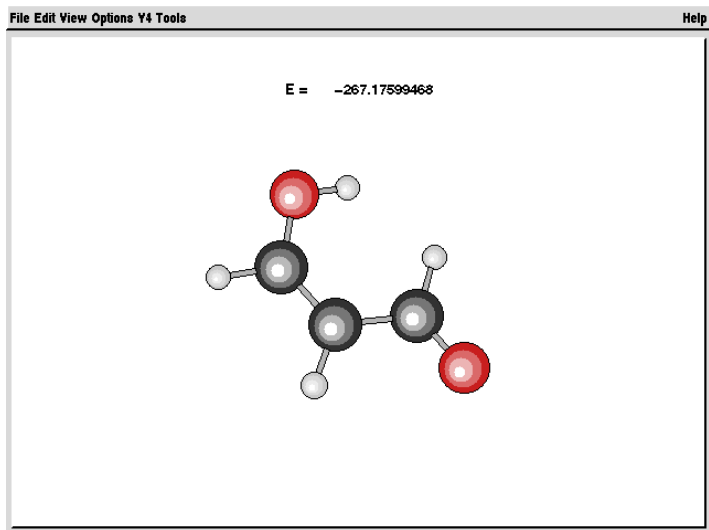
Malon-0



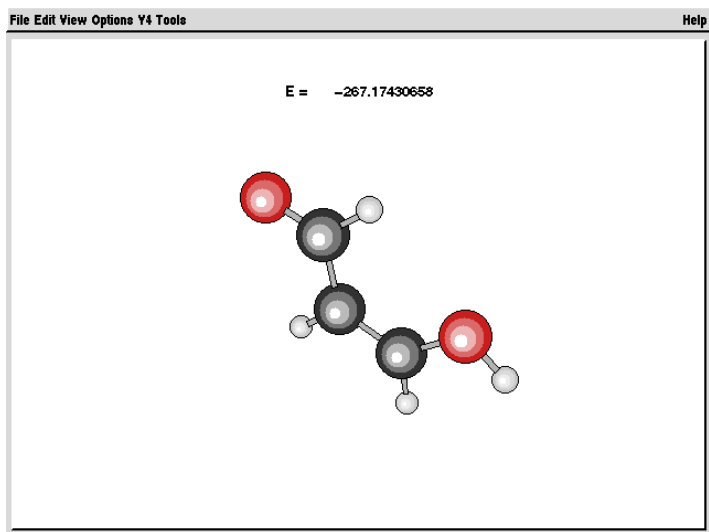
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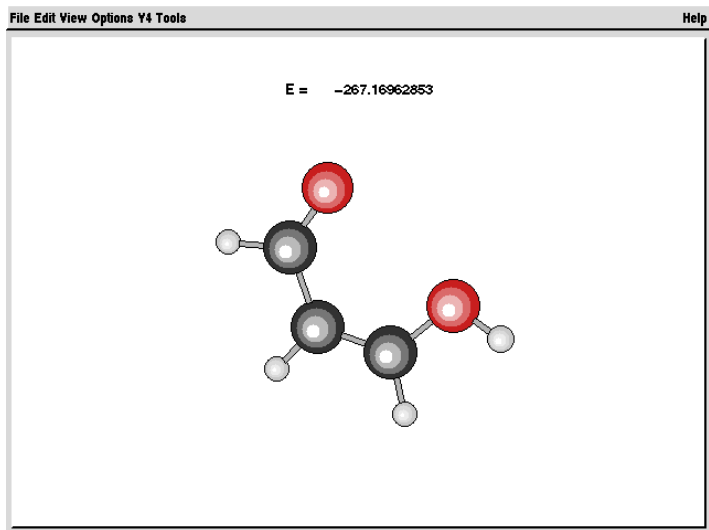
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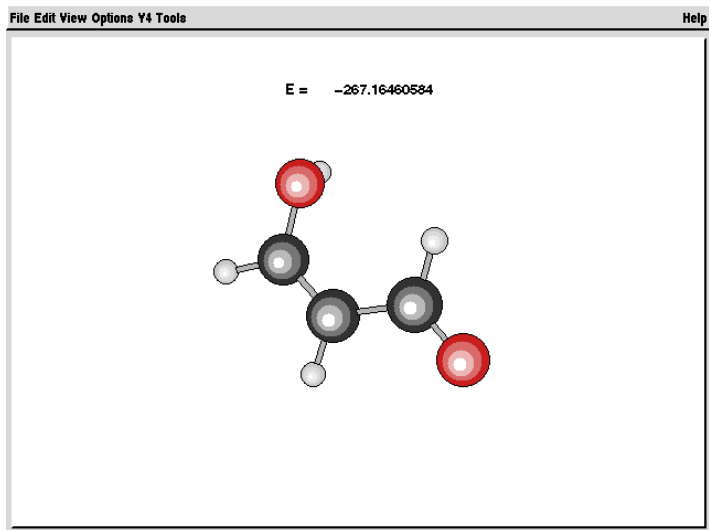
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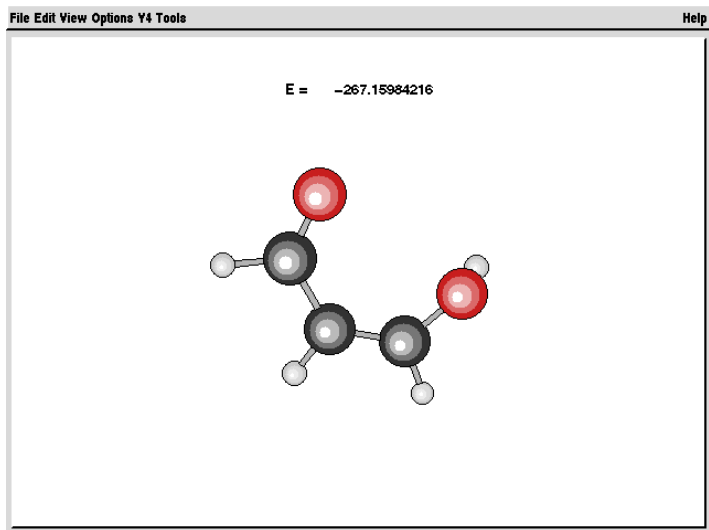
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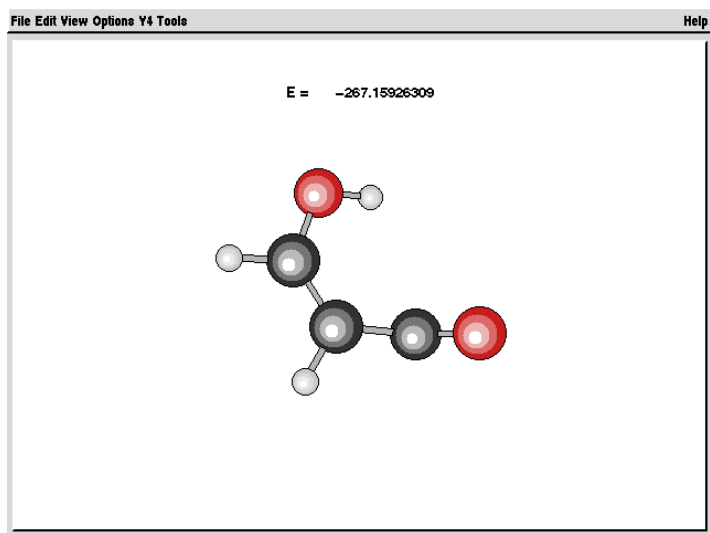
Malon-5



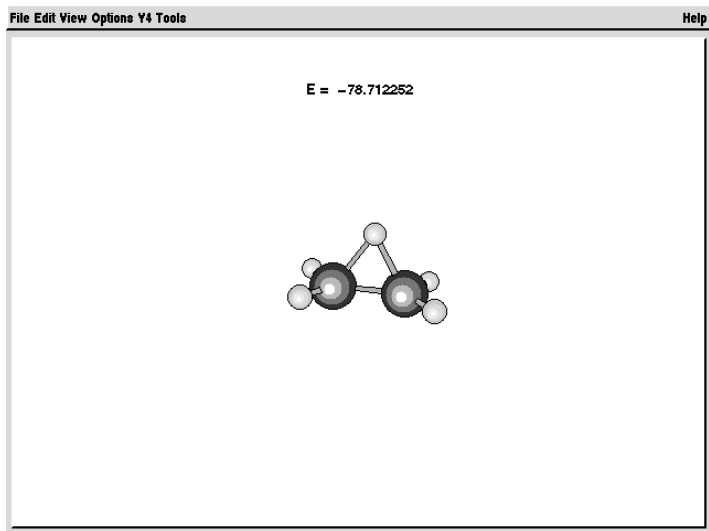
Malon-6



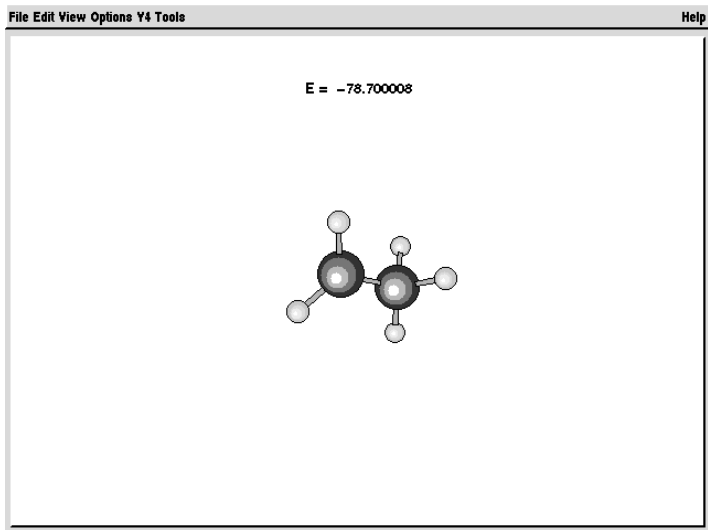
Malon-7



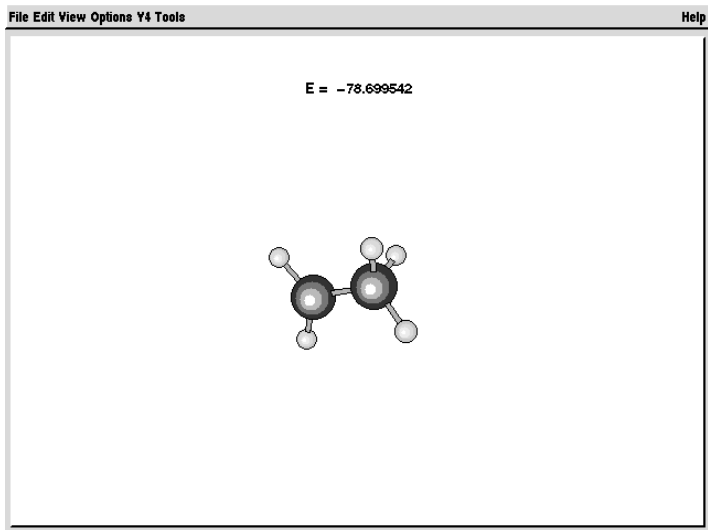
$C_2H_5^+$ min



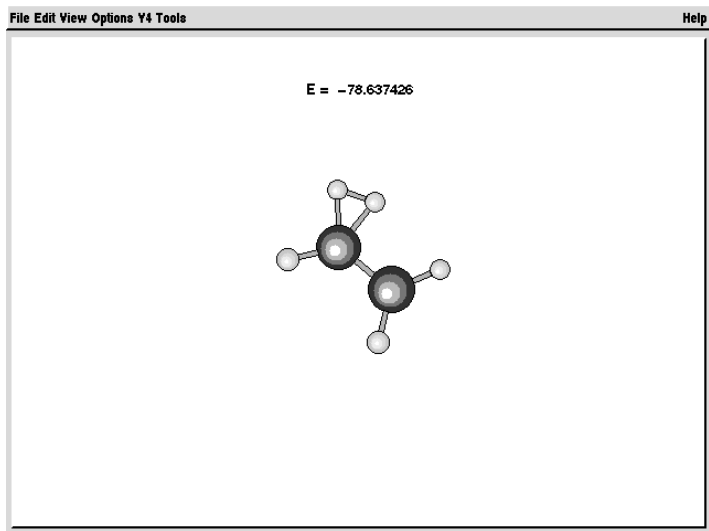
$C_2H_5^+$ ts1



$C_2H_5^+$ ts2



$C_2H_5^+$ ts3



Outlook

Secure: Construction of the C_mH_n , $C_mH_n^+$ ground state surfaces, $m + n \leq 8$.

More work: MULTIMODE analysis, thermal spectra (not spectroscopic accuracy).

More work yet: Cross-sections (suitably resolved) on a ground state surface; e.g., $H + C_2H_4^+ \leftrightarrow H_2 + C_2H_3^+$.

Not secure: Excited state surfaces, coupling coefficients, associated cross sections; e.g., $H + C_2H_4^+ \leftrightarrow H^+ + C_2H_4$.