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Global analytical potential energy surfaces: Searching for symmetry adapted functional forms

Outline

1) General concepts

2) Analytical Forms for XY_n type of molecules

3) Application to CH_4 and NH_3

4) Analytical Forms for adsorption processes $AB \rightarrow AB/M$

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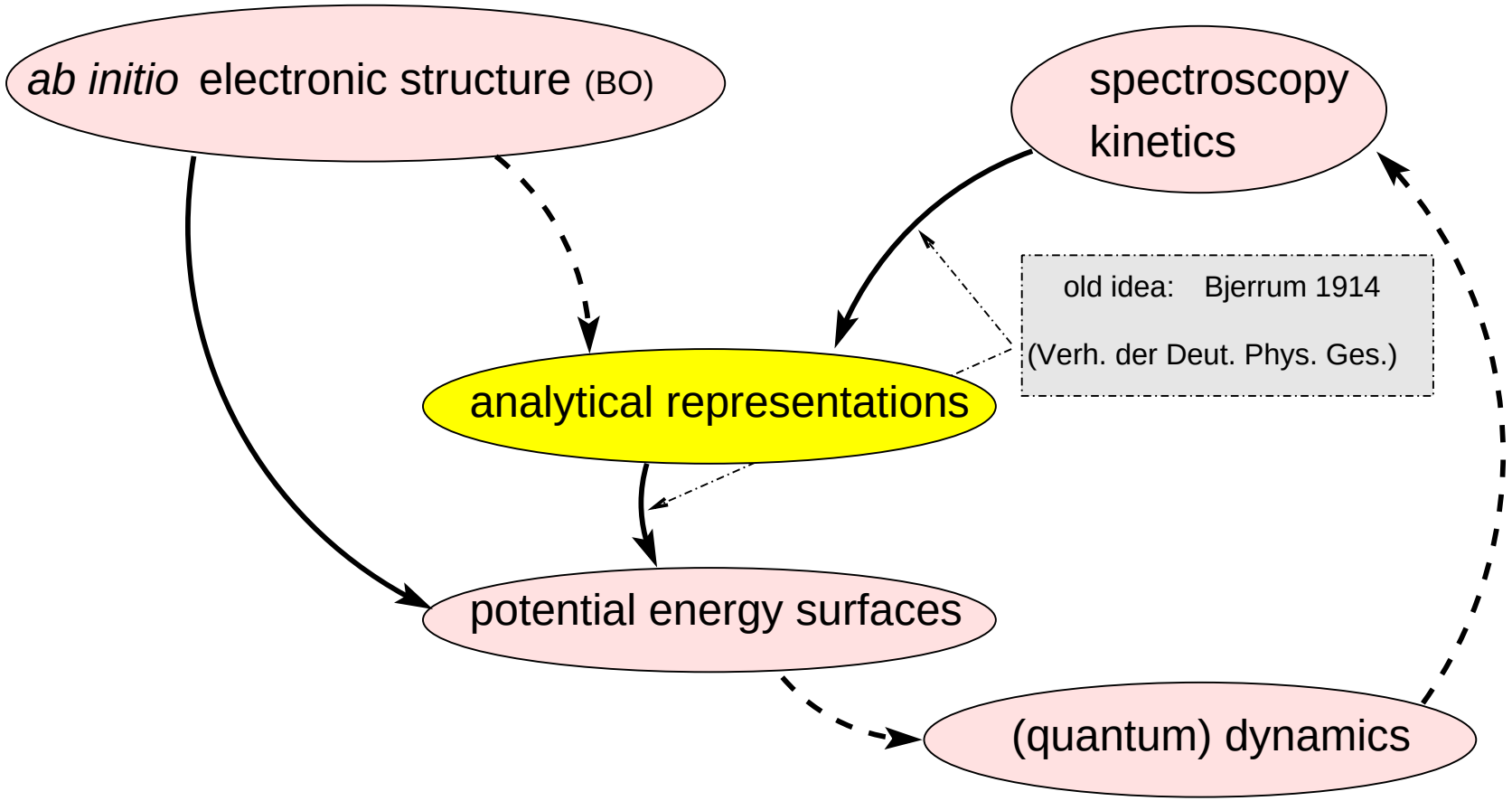
Roar A. Olsen,	Leiden University (new address as from Sep 2008: Akershus University College, Norway)

General concepts related to PES

PES flowchart



Methods

ab initio calculation:

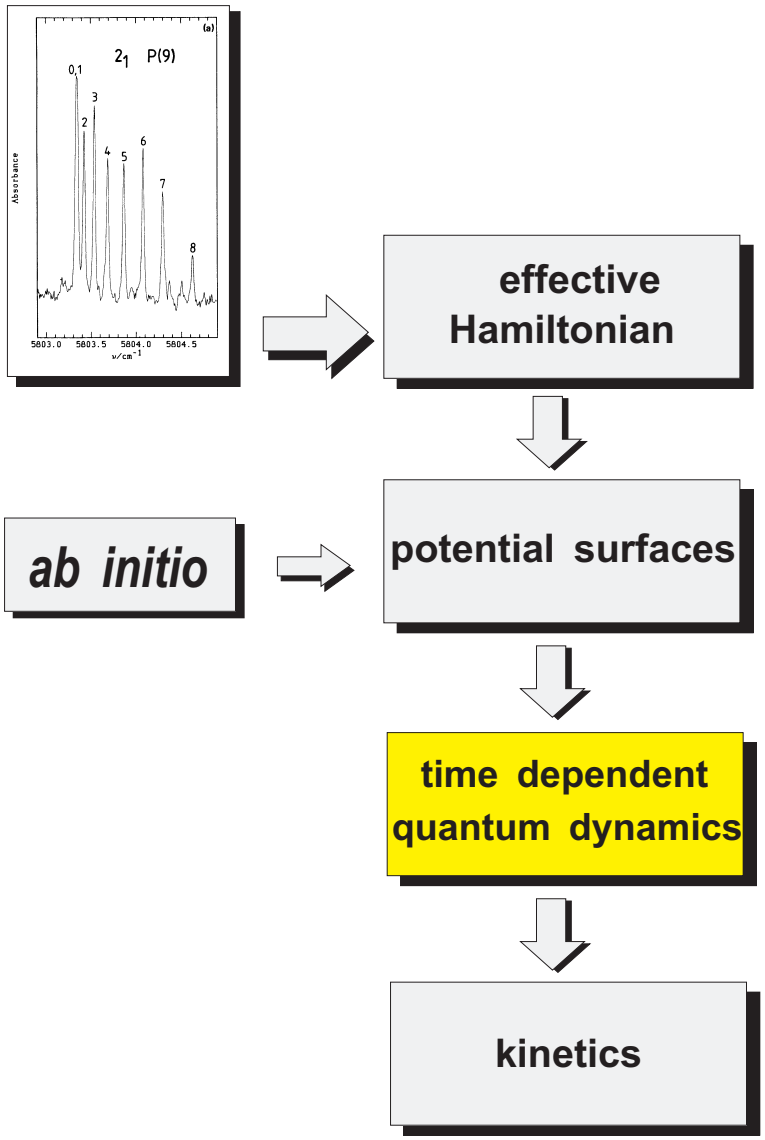
CASPT2, CCSD(T), MRCI, DFT

Dynamics:

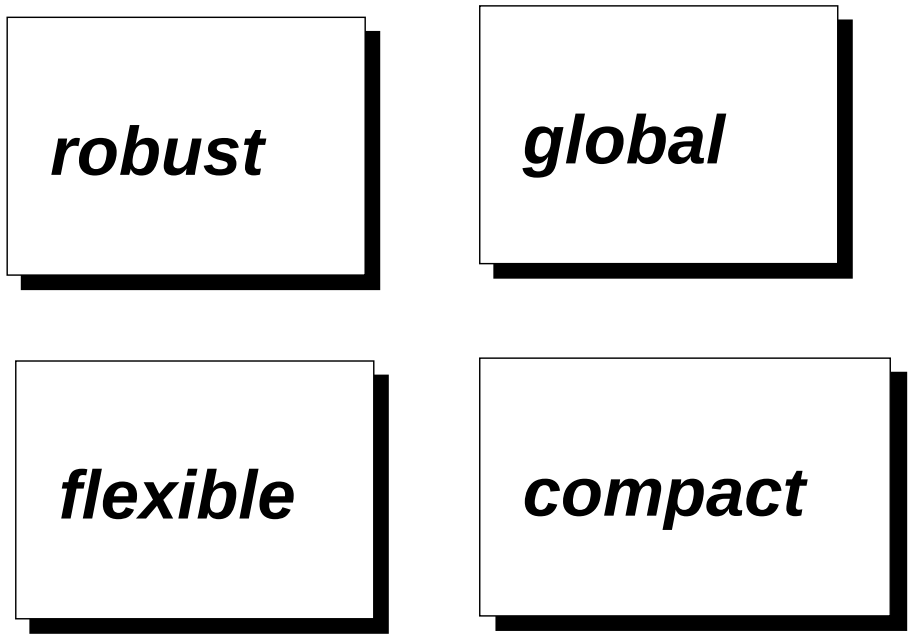
$$\Psi(t,\boldsymbol{r}) = \sum_{n}^{N} \underbrace{b_n(t)}_{\text{time}} \underbrace{\Phi_n(\boldsymbol{r})}_{\text{space}}$$

$$\boldsymbol{b}(t) = \boldsymbol{U}(t,t_0)\,\boldsymbol{b}(t_0)$$

$\Phi_n(\boldsymbol{r})$: spectroscopic states



Analytical PES criteria



choice of coordinates

coordinates for dynamical calculations

unique description of configuration space

representation of kinetic energy

Examples:

- cartesian coordinates of position vectors ($\boldsymbol{x}$)
- normal coordinates
- Jacobi or Radau type of coordinates

coordinates for PES representation

related to interatomic interactions

symmetry advantage (permutation-inversion)

Examples:

- interatomic distances (r_{ij})
- valence bond elongation and angles

($\boldsymbol{x}(r_{ij})$ does not exist for all r_{ij})

XY_n-type PES

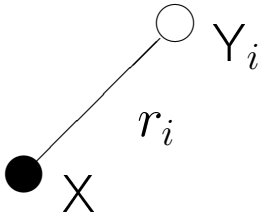
PES as positive definite sum of stretching and bending potentials

$$V = \underbrace{V_{s(XY)} + V_{s(YY)}}_{\text{two-body terms}} + \underbrace{V_{b(YXY)}}_{\text{three-body term}}$$

reference energy at stable equilibrium molecular structure

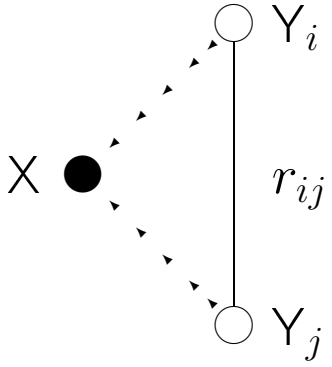
Stretching potentials

$$V_{s(XY)} = \sum_{i=1}^{n} v_{s(XY)}(r_i)$$



$v_{s(XY)}(r_i) \sim$ Morse-type

$$V_{s(YY)} = \sum_{i>j=1}^{n} v_{s(YY)}(r_{ij})$$



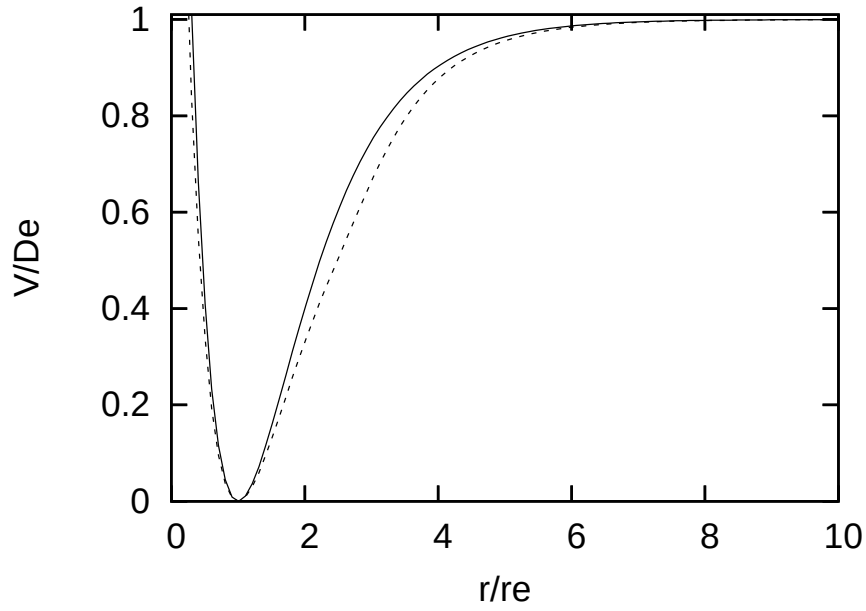
$n \geq 6$ for neutral dissociation

$$v_s(r) = \frac{1}{2} f_s \left(\frac{1 - \exp(-a_s[r - r_e])}{a_s} \right)^2 \left(1 + \sum_n \epsilon_n \exp(- \left(\frac{r_n}{r} \right)^n) \right)^2$$

Examples: $n = 6$

—— $\epsilon_6 = 0.0$

- - - $\epsilon_6 = 0.1$
$r_6 = 3\, r_e$



Marquardt and Quack, *JCP 109* (**1998**)

Switching upon bond dissociation

$$V_{s(XY)} = \sum_{i=1}^{n} \overbrace{v_{s(XY)}(r_i)}^{f_s, a_s, r_e, \ldots} \qquad (\mathsf{XY_n})$$

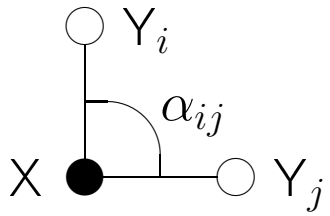
$$V_{s(XY)} \overset{r_n \to \infty}{=} \sum_{i=1}^{n-1} \underbrace{v_{s(XY)}(r_i)}_{f'_r, a'_s, r'_e, \ldots} + D_e \qquad (\mathsf{XY_{n-1}})$$

parameters are smoothly varying functions of bond distances $p = p(r_1, r_2, \ldots)$

$p' = p(\ldots, r_k \to \infty, \ldots)$

Bending potentials

$$V_b(\alpha) = \frac{1}{2} f_b (\alpha - \alpha_e)^2$$



Anharmonicity ?

$$\Rightarrow V_b(\alpha) = \frac{1}{2} f_b (\alpha - \alpha_e)^2 + \sum_{k \geq 3} a_{b_k} (\alpha - \alpha_e)^k$$

Ensure positive definiteness ?

$$\Rightarrow V_b(\alpha) = \frac{1}{2} f_b \left(\underbrace{\sum_{k=1}^{K} a_{b_k} (\alpha - \alpha_e)^k}_{\text{polynomial expansion}} \right)^2 \overset{\alpha \to \alpha_e}{\approx} \frac{1}{2} f_b (\alpha - \alpha_e)^2$$

Bending hypersurfaces in polyatomic molecules ?

idea: use polynomial expansions of symmetry adapted forms

suppose bending space is reducible in irreductible representations $1, 2, \ldots$ in the equilibrium structure point group symmetry

$$V_b = \frac{1}{2} f_{b_1} \left(\sum_{k=1}^{K} a_{b_k}^{(1)} s_k^{(1)} \right)^2 + \frac{1}{2} f_{b_2} \left(\sum_{k=1}^{K} a_{b_k}^{(2)} s_k^{(2)} \right)^2 + \ldots$$

symmetry adapted forms $s_k^{(i)}$ from reduction in the tensor spaces

Example 1 The bending space of NH_3 is $3D$ and at $k = 4$, a $81D$ space must be reduced. Result of the reduction is

$$4\,A_1 \oplus A_2 \oplus 5\,E$$

spanning a $15D$ space of non-vanishing expressions.

E-forms of power 4 that might be obtained are

$$\boldsymbol{s}^{(E)}_{4_4} = \begin{cases} s^{(E)}_{4_4}(a) = s^{(E)}_1(a)^4 - s^{(E)}_1(b)^4 \\ s^{(E)}_{4_4}(b) = -2s^{(E)}_1(a)^3 s^{(E)}_1(b) - 2s^{(E)}_1(a) s^{(E)}_1(b)^3 \end{cases}$$

$$\boldsymbol{s}^{(E)}_{4_5} = \begin{cases} s^{(E)}_{4_5}(a) = s^{(E)}_1(a)^4 - 6\, s^{(E)}_1(a)^2 s^{(E)}_1(b)^2 + s^{(E)}_1(b)^4 \\ s^{(E)}_{4_5}(b) = 4s^{(E)}_1(a)^3 s^{(E)}_1(b) - 4s^{(E)}_1(a) s^{(E)}_1(b)^3 \end{cases}$$

Marquardt *et al*, *JPC 109* (**2005**)

Example 2 The bending space of CH_4 is $6D$ and at $k = 3$, a $216D$ space must be reduced. Result of the reduction is

$$6\,A_1 \oplus 2\,A_2 \oplus 6\,E \oplus 8\,F_1 \oplus 4\,F_2$$

spanning a $56D$ space of non-vanishing expressions of power 3.

Complete reduction studies are necessary in order to guarantee maximum flexibility at a given expansion order.

Reduction may become very tedious in high dimensional spaces.

This lead to the development of a fully automatic, fully symbolic computer algebra program using `MAPLE`.

Marquardt and Sagui, *Mol. Phys.* 105 (2007)

Non-linear adjustement methods

Levenberg-Marquardt algorithm to minimize $\chi^2 = \sum_i \left(V_i^{\text{real}} - V_i^{\text{model}}\right)^2$

Extended algorithm to minimize $\chi^2 + \sum_k \lambda_k C_k$ "new"

(Marquardt and Quack, *JCP* 109 (1998))

C_k: additional non-linear conditions.

Example 1: XY bond dissociation energy

$$C = \underbrace{\frac{f_s}{2\,a_s^2}\left(1 + \sum_n \epsilon_n\right)^2}_{D_e} - D_e^{\text{"exp"}}$$

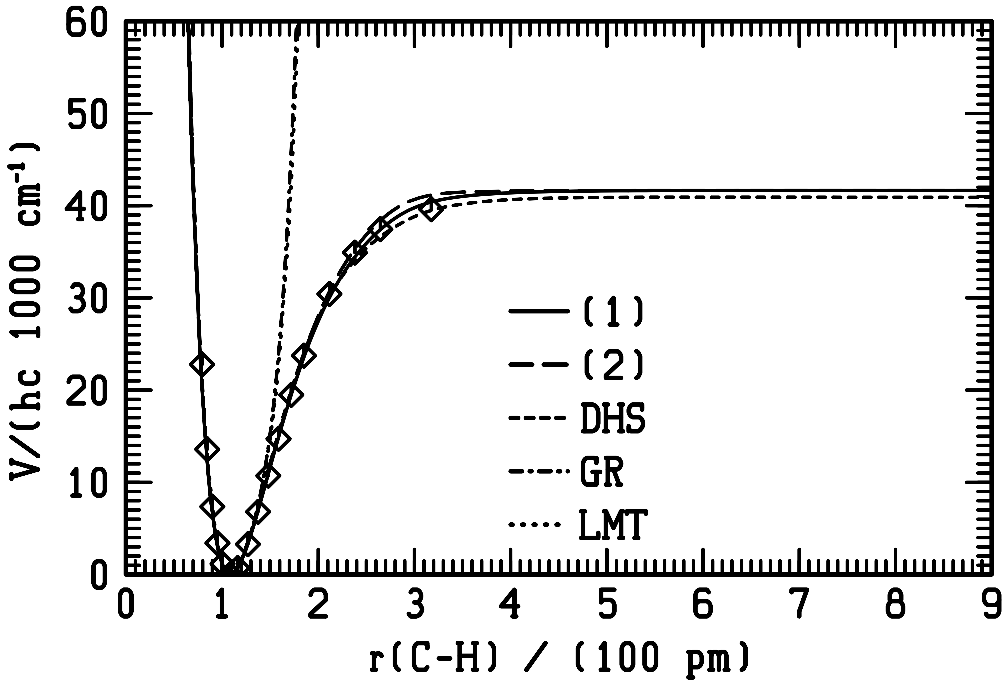
Example 2: NH_2 barrier to linearity in the asymptotic limit $NH_2 + H$ (Renner-Teller problem).

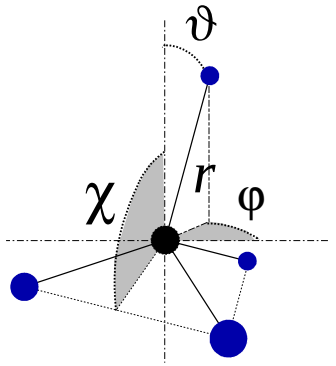
The analytical expression for the barrier height is

$$
\begin{aligned}
E_{\mathrm{barr}}(NH_2) \;=\; & \mathrm{Fb1}_{\,2}\Big[1/3\ \mathrm{AB1}_{\,1,1,2}(-1-\mathrm{ce}_{\,2})\sqrt{3}+1/3\ \mathrm{AB1}_{\,2,1,2}(-1-\mathrm{ce}_{\,2})^2+2/3\ \mathrm{AB1}_{\,2,2,2}(-1-\mathrm{ce}_{\,2})^2+1/9\ \mathrm{AB1}_{\,3,1,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{3}+2/9\ \mathrm{AB1}_{\,3,2,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{3} \\
& +2/9\ \mathrm{AB1}_{\,3,3,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{6}+1/9\ \mathrm{AB1}_{\,4,1,2}(-1-\mathrm{ce}_{\,2})^4+2/9\ \mathrm{AB1}_{\,4,2,2}(-1-\mathrm{ce}_{\,2})^4+\frac{2}{27}\ \mathrm{AB1}_{\,4,3,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{6}\sqrt{3}+4/9\ \mathrm{AB1}_{\,4,4,2}(-1-\mathrm{ce}_{\,2})^4\Big]^2 \\
& +\mathrm{Fb2}_{\,2}\Big[\Big(-1/6\ \mathrm{AB2}_{\,1,1,2}(-1-\mathrm{ce}_{\,2})\sqrt{6}-1/18\ \mathrm{AB2}_{\,2,1,2}(-1-\mathrm{ce}_{\,2})^2\sqrt{6}\sqrt{3}-1/6\ \mathrm{AB2}_{\,2,2,2}(-1-\mathrm{ce}_{\,2})^2-1/18\ \mathrm{AB2}_{\,3,1,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{6}-1/18\ \mathrm{AB2}_{\,3,2,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{3} \\
& -1/9\ \mathrm{AB2}_{\,3,3,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{6}-\frac{1}{54}\ \mathrm{AB2}_{\,4,1,2}(-1-ce_2)^4\sqrt{6}\sqrt{3}-1/18\ \mathrm{AB2}_{\,4,2,2}(-1-\mathrm{ce}_{\,2})^4-1/27\ \mathrm{AB2}_{\,4,3,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{6}\sqrt{3}-2/9\ \mathrm{AB2}_{\,4,4,2}(-1-\mathrm{ce}_{\,2})^4 \\
& -2/9\ \mathrm{AB2}_{\,4,5,2}(-1-\mathrm{ce}_{\,2})^4\Big)^2+\Big(-1/2\ \mathrm{AB2}_{\,1,1,2}(-1-\mathrm{ce}_{\,2})\sqrt{2}-1/6\ \mathrm{AB2}_{\,2,1,2}(-1-\mathrm{ce}_{\,2})^2\sqrt{2}\sqrt{3}-1/12\ \mathrm{AB2}_{\,2,2,2}(-1-\mathrm{ce}_{\,2})^2\sqrt{6}\sqrt{2}-1/6\ \mathrm{AB2}_{\,3,1,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{2} \\
& -1/36\ \mathrm{AB2}_{\,3,2,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{6}\sqrt{2}\sqrt{3}-1/3\ \mathrm{AB2}_{\,3,3,2}(-1-\mathrm{ce}_{\,2})^3\sqrt{2}-1/18\ \mathrm{AB2}_{\,4,1,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{2}\sqrt{3}-1/36\ \mathrm{AB2}_{\,4,2,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{6}\sqrt{2}-1/9\ \mathrm{AB2}_{\,4,3,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{} \\
& -1/9\ \mathrm{AB2}_{\,4,4,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{6}\sqrt{2}-1/9\ \mathrm{AB2}_{\,4,5,2}(-1-\mathrm{ce}_{\,2})^4\sqrt{6}\sqrt{2}\Big)^2\Big] \\
& +\mathrm{Dii}_{\,2}\left(e^{-\,\mathrm{aii}_{\,2}\,\mathrm{re}_{\,2}\sqrt{2}[\sqrt{2}-\sqrt{1-\mathrm{ce}_{\,2}}]}-1\right)^2
\end{aligned}
$$

Applications: CH_4

Stretching potential

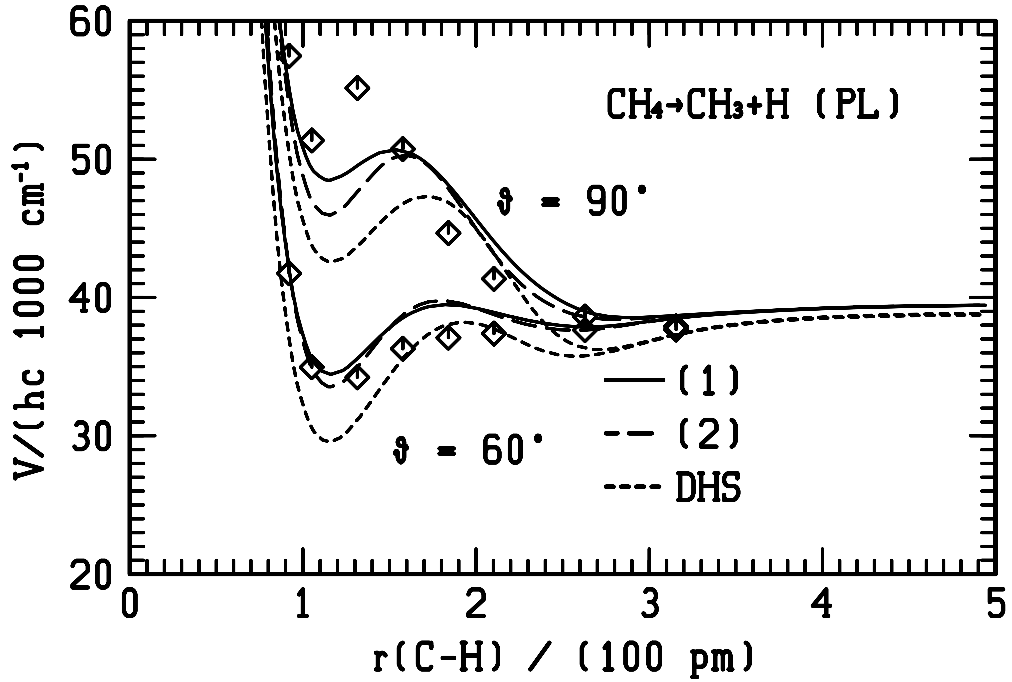




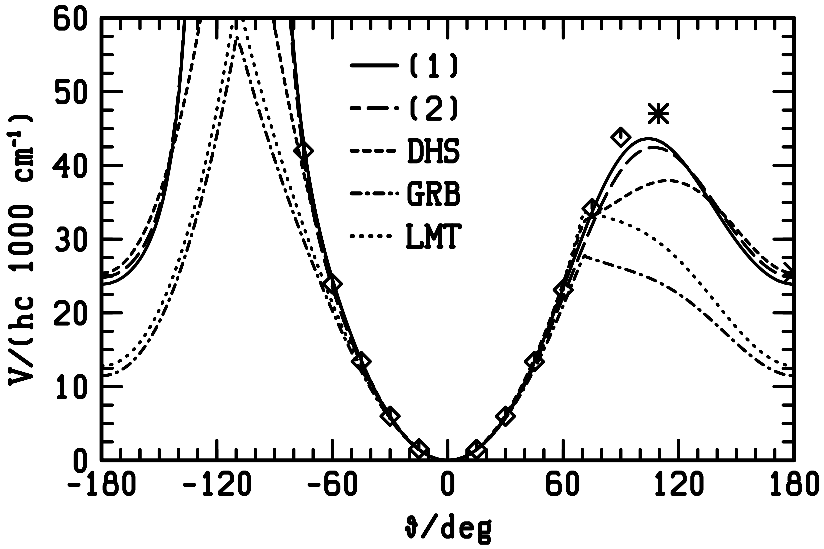
◇ *ab initio* data MR-SDCI

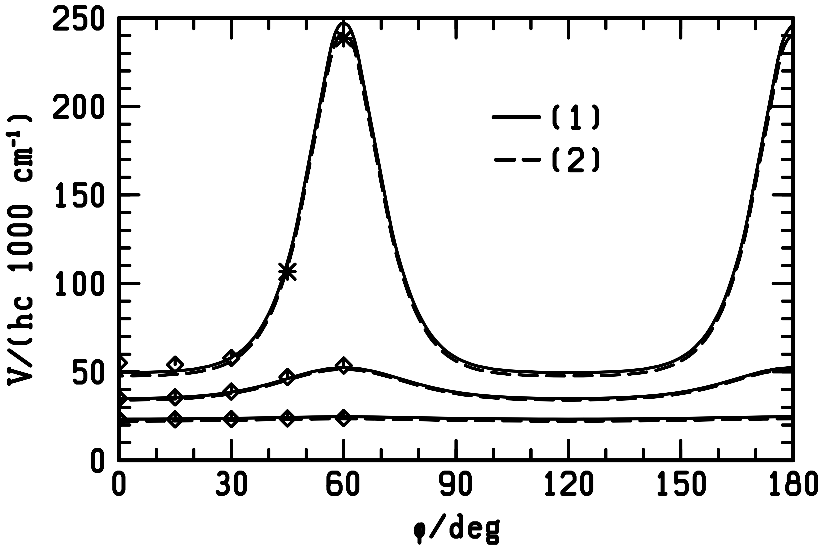
Marquardt and Quack, *J. Chem. Phys.* 109 (1998)
Marquardt and Quack, *J. Phys. Chem. A* 108 (2004)

CH stretching potential in highly distorted CH_4



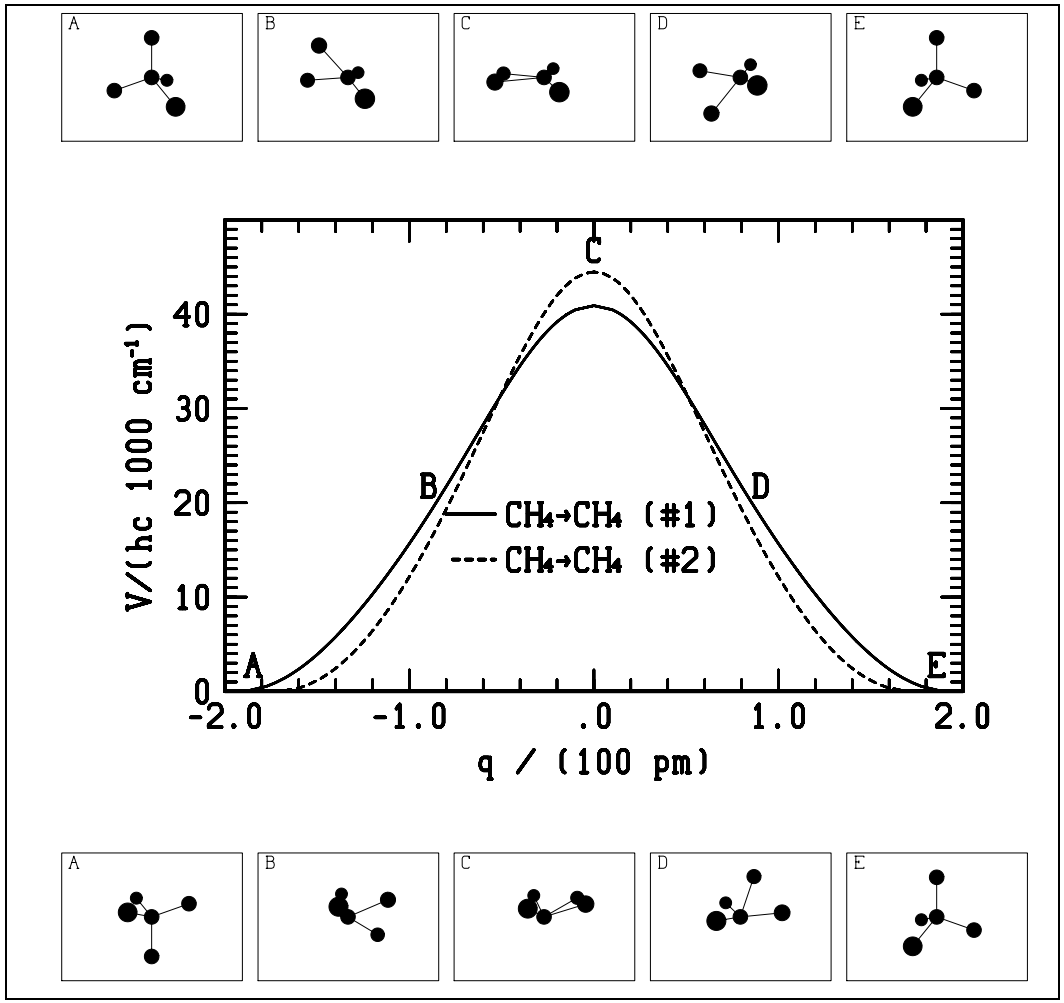
Bending potentials for large amplitude distortions in CH_4





Marquardt and Quack, *J. Phys. Chem. A* 108 (2004)

Methane inversion



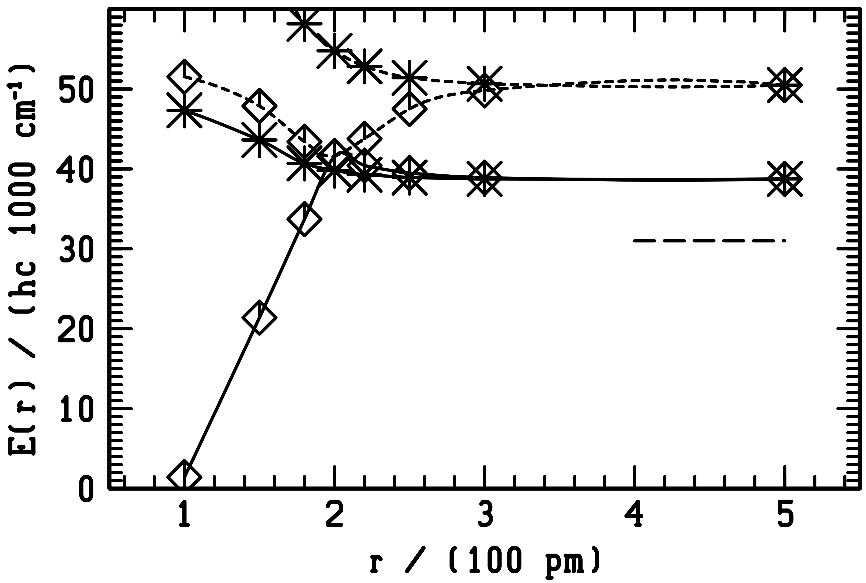
Applications: NH_3

NH_3 dissociation channels (octade)

– – $NH_3(^1A_1) \longrightarrow NH(^3\Sigma^-) + H_2(^1\Sigma_g^+)$,
$\Delta_r H_0^\ominus \approx 414$ kJ mol^{-1}

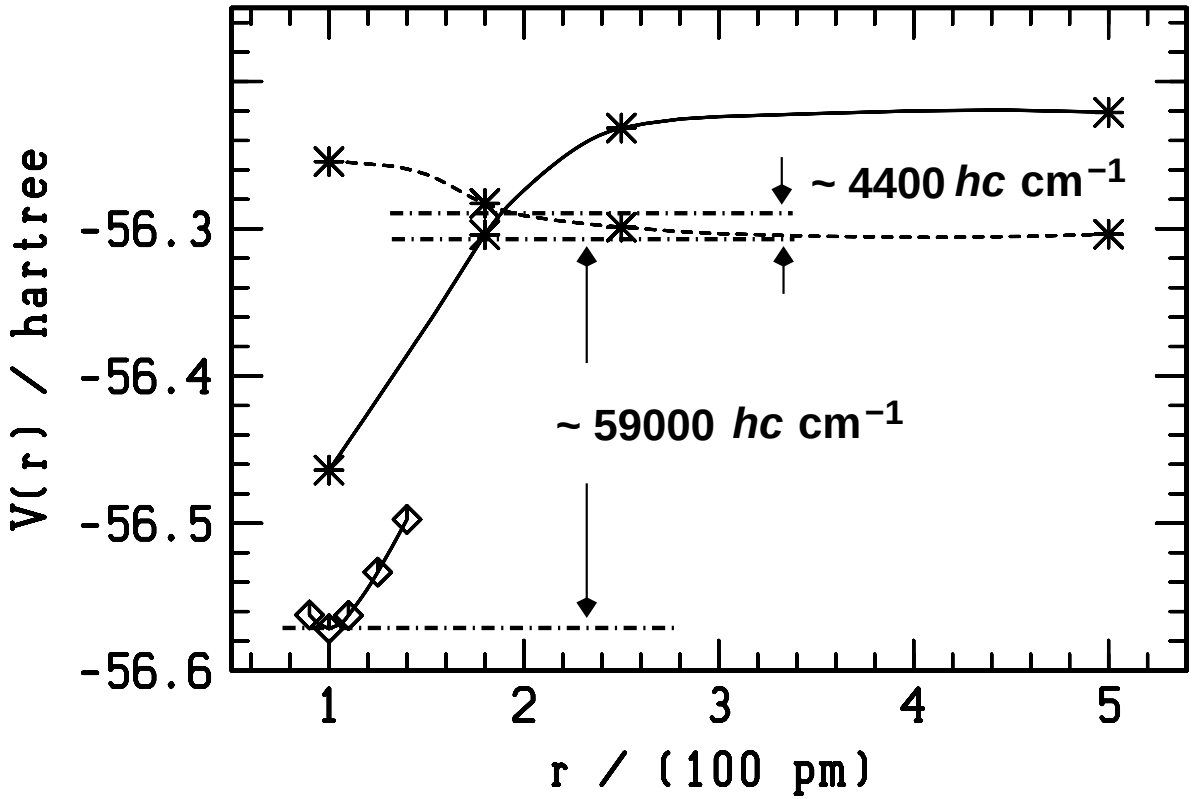
—— $NH_3(^1A_1) \longrightarrow NH_2(^2B_1) + H(^2S_{(1/2)})$,
$\Delta_r H_0^\ominus \approx 448$ kJ mol^{-1}

- - - $NH_3(^1A_1) \longrightarrow NH_2(^2A_1) + H(^2S_{(1/2)})$,
$\Delta_r H_0^\ominus \approx 590$ kJ mol^{-1}

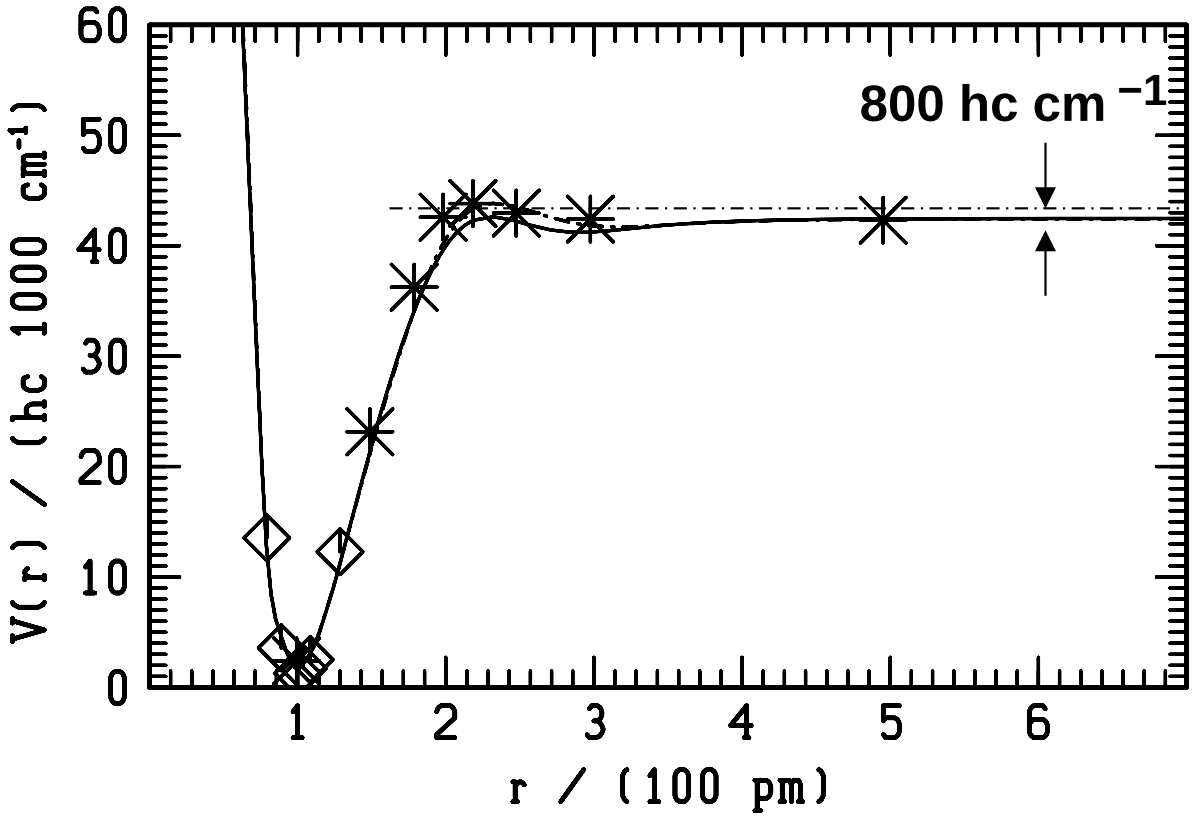


◇ singlet ∗ triplet

Merging of CCSD(T) CBS ($\diamond$) and MR-CI VTZ ($*$) data

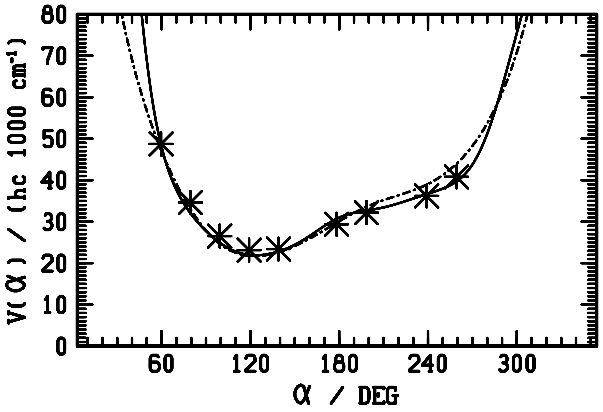


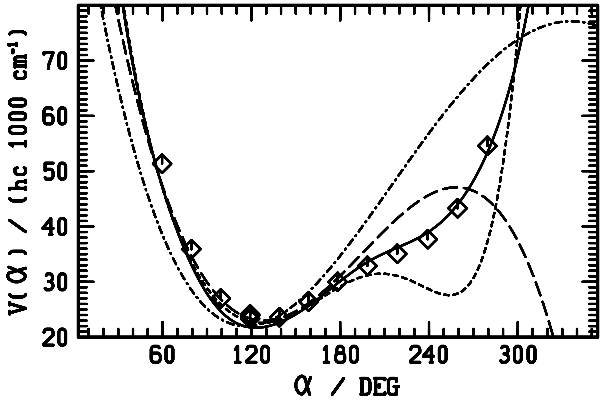
Results: 1D $V(r_{\mathrm{NH}})$, planar ammonia



Results: 1D $V(\alpha)$, planar ammonia

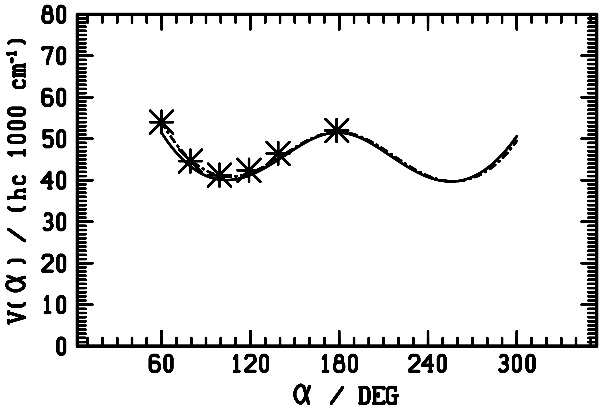
$r = 150$ pm

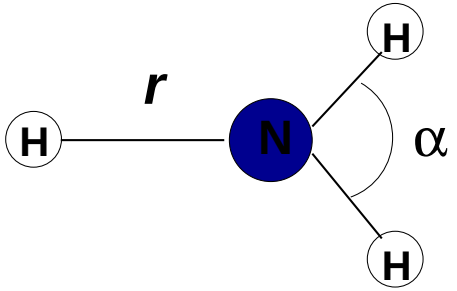




Marquardt *et al*, *JPC B* 109 (2005)

$r = 300$ pm





number of parameters

*31	APOT3	Marquardt *et al JPC B* 109 (2005)	global
84	LTYCJ	Lin *et al JCP* 117 (2002)	semi-global
91	LCH	Leonard *et al CPL* 370 (2003)	local
812	RMH	Rajamäki *et al JCP* 118 (2003)	local

* with 10 additional, non-linear conditions among these parameters

Vibrational term values NHD_2 (in cm^{-1})

Sym	Levels	Experiment[1]	Theory			
			RMH[2]	APOT2[3]	APOT4[4]	APOT4[5]
A^-	$(0)^u$	0.171	0.17	0.13	0.16	0.16
A^+	$(2^1)^l$	810.23	810.22	835.07	808.81	808.82
A^-	$(2^1)^u$	819.56	819.58	843.19	817.52	817.53
A^+	$(4_a{}^1)^l$	1233.37	1233.11	1256.16	1234.29	1234.31
A^-	$(4_a{}^1)^u$	1235.89	1235.65	1258.30	1236.71	1236.73
		⋮	⋮	⋮	⋮	⋮
B^+	$(4_b{}^1)^l$	1461.79	1461.57	1483.36	1461.48	1461.49
B^-	$(4_b{}^1)^u$	1461.99	1461.78	1483.47	1461.65	1461.65
		⋮	⋮	⋮	⋮	⋮
A^+	$(3_a{}^1)^l$	2430.80	2430.11	2442.80	2435.43	2435.47
A^-	$(3_a{}^1)^u$	2434.62	2434.07	2443.98	2437.09	2437.13
		⋮	⋮	⋮	⋮	⋮
B^+	$(3_b{}^1)^l$	2559.81	2557.99	2553.08	2564.11	2564.15
B^-	$(3_b{}^1)^u$	2559.96	2558.14	2553.18	2564.22	2564.26
		⋮	⋮	⋮	⋮	⋮
A^-	$(1^1)^l$	3404.24	3407.10[e]	3399.59	3406.27	3406.24
A^+	$(1^1)^u$	3404.32	3407.35[f]	3403.31	3406.33	3406.30
		⋮	⋮	⋮	⋮	⋮

[1] Snels *et al*, *J. Chem. Phys.* **119** (2003)

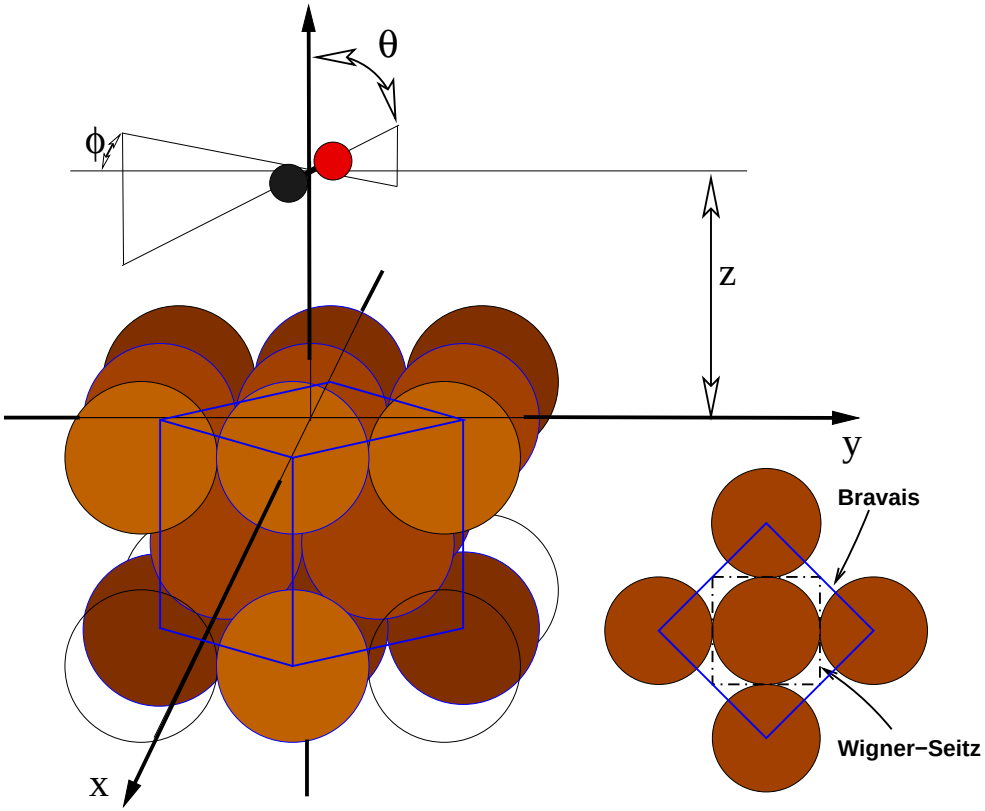
[2] Rajamäki *et al*, *J. Chem. Phys.* **118** (2003)

[3] Marquardt *et al*, *J. Phys. Chem.*B **109** (2005)

[4] Marquardt *et al*, *to be pub.* calculation D. Luckhaus

[5] Values MCTDH (F. Gatti)

CO/Cu(100) PES



essentially 6D problem:
r, θ, ϕ, x, y, z

prototype system for (non-dissociative) adsorption processes, but only one analytical, semi-empirical PES representation:
Tully *et al*, *J. Vac. Sci. Techn. A* (1993)

cluster vs slab type calculations

zero coverage PES?
lateral diffusion barrier?
periodicity at Wigner-Seitz boundary?

Generic analytical forms AB/M

2 body potentials

$$V \approx \sum_M \quad V_{\mathrm{A}M}(|\,\boldsymbol{r}_{\mathrm{A}} - \boldsymbol{r}_M\,|)$$
$$+\; V_{\mathrm{B}M}(|\,\boldsymbol{r}_{\mathrm{B}} - \boldsymbol{r}_M\,|)$$
$$+\; V_{\mathrm{AB}M}(\boldsymbol{r}_{\mathrm{A}} - \boldsymbol{r}_M, \boldsymbol{r}_{\mathrm{B}} - \boldsymbol{r}_M)$$

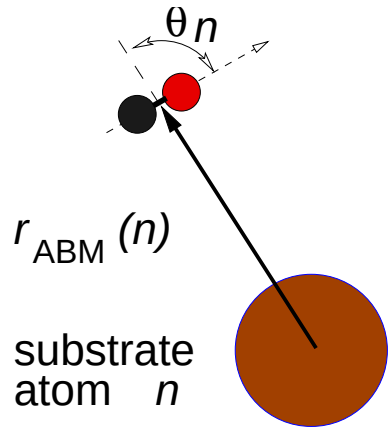
3 body potential

$$+ \quad V_{\mathrm{AB}}(|\boldsymbol{r}_{\mathrm{A}} - \boldsymbol{r}_{\mathrm{B}}|)$$

Generic analytical forms AB/M: 2 body and 3 body potentials

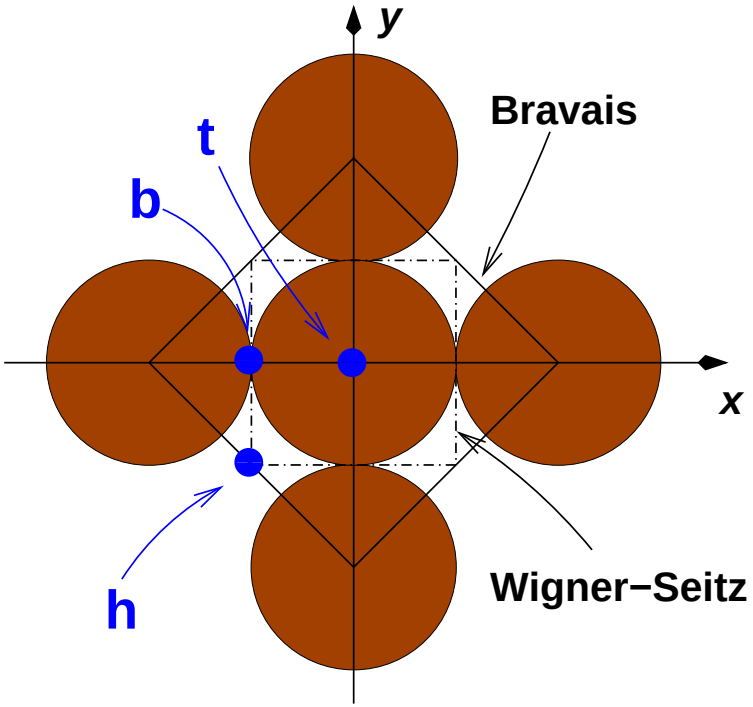
$$V_{XM}(r) = D_{XM}\left[\exp(-2\,A_{XM}[r - R_{XM}]) - 2\,C_{XM}\exp(-A_{XM}[r - R_{XM}])\right]$$

$$\begin{aligned} r &= r_{\mathrm{ABM}}(n) \\ c &= \cos(\theta_n) \end{aligned}$$



$$V_{\mathrm{ABM}}(r,c) = D_{\mathrm{ABM}} \sum_{\ell=0}^{N_{\mathrm{leg}}} W_\ell\, P_\ell(c)\, R_\ell(r)$$

$$R_\ell(r) = \exp\left(-\left(\frac{R_{\mathrm{ABM}}^{(\ell)}}{r}\right)^6\right) - 1$$



Some potential parameters vary *slowly* as a function of the positions x and y parallel to the substrate, and perpendincularly along z.

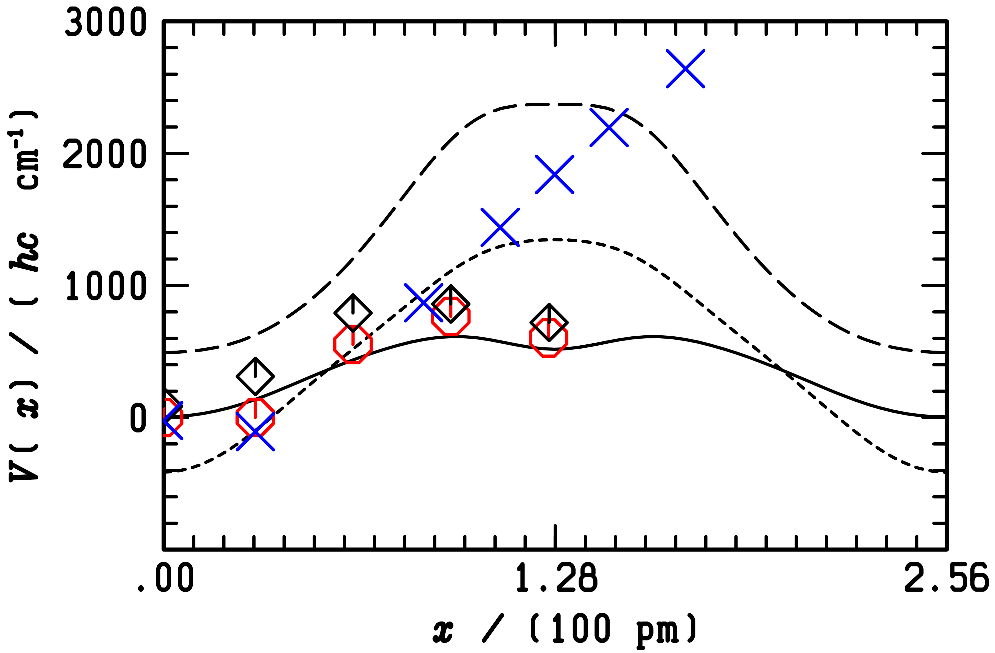
$$\begin{aligned} p(x,y) &= p_{\mathsf{t}}\ c(x)\ c(y) \\ &+ p_{\mathsf{b}}\ (c(x)\ s(y) + s(x)\ c(y)) \\ &+ p_{\mathsf{h}}\ s(x)\ s(y) \end{aligned}$$

$$\begin{aligned} c(x) &= \cos^2(\frac{\pi\ x}{a}) \\ s(x) &= \sin^2(\frac{\pi\ x}{a}) \\ &= 1 - c(x) \end{aligned}$$

$$a = \text{Wigner Seitz lattice parameter}$$

Discussion on the CO/Cu(100) PES

Lateral diffusion potential



——— this work

◇, ○ slab calculations ADF
Becke-Perdew GGA, VWN-LDA
TZIP basis
Fouquet *et al*,
J. Chem. Phys. **119** (2003)

× cluster calculations MOLPRO
many different cluster sizes
TH3 functional (Tozer and Handy)
cc-pVTZ basis

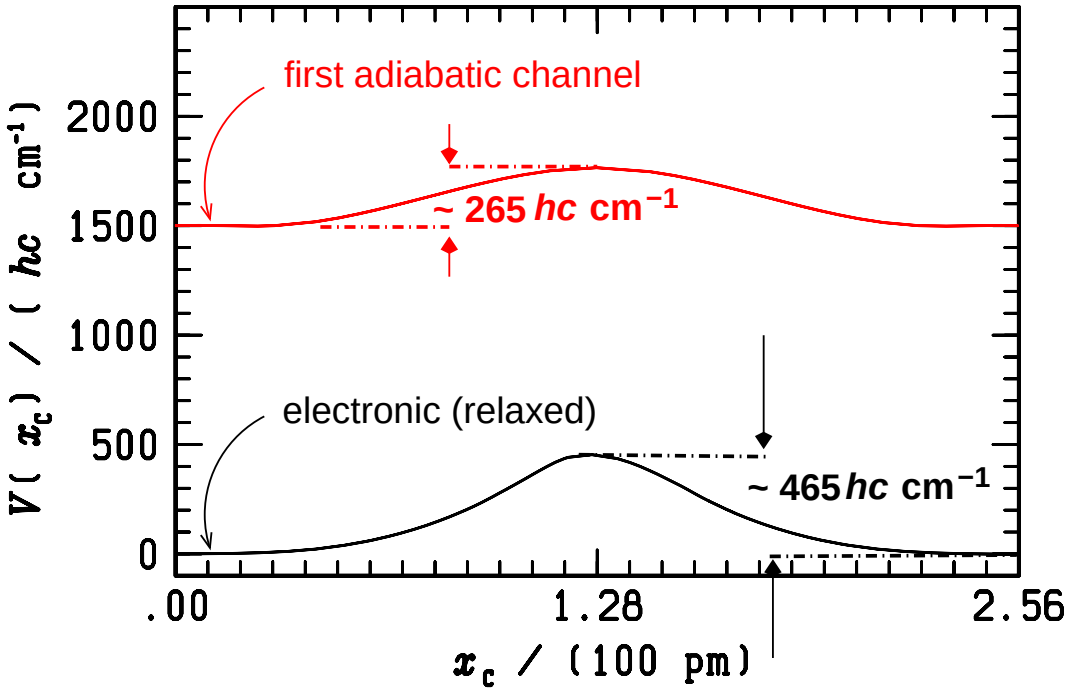
– – – – Tully *et al*,
J. Vac. Sci. Techn. A (1993)

- - - - - - representation from Tully *et al*,
adjusted (this work)

Lateral diffusion barrier

Theory

$\sim 265\ hc\,\mathrm{cm}^{-1}$



Experiment (HAS)

$30\ \mathrm{meV} \approx 240\ hc\,\mathrm{cm}^{-1}$

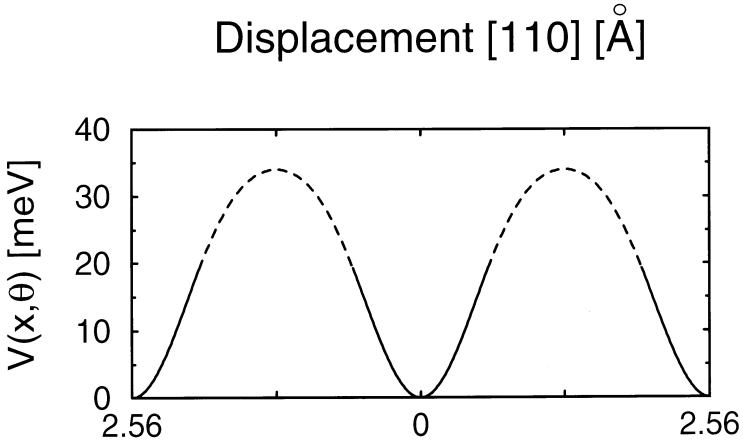


Figure adapted from
Graham and Toennies,
Surf. Sci. **427** (1999)

Harmonic Vibrational Wavenumbers (in cm^{-1})

label	present work		THG		exp [3]
	harmonic		*harmonic*[1]	*anharmonic*[2]	
CO stretch (A)	2066	2069	2179 2180	2150	2079
CO adsorption (A)	320	384	*310* *372*	345	345
CO frust rot (E)	299	304	*362* *357*	335	285
CO frust tra (E)	8	6	4 4	27	32

2nd row: inclusion of Cu vibrations

[1] Tully *et al*, *J. Vac. Sci. Techn. A* (1993)

[2] Tremblay *et al*, *J. Chem. Phys.* (2008)

[3] Graham *et al*, *J. Chem. Phys.* (1998)

Conclusions

Analytical, global representations of multidimensional PES are useful but still challenging.

Generic form of compact, global PES for XY_n due to new , unconventional functional forms. Important advantage of using symmetry.

CH_4 and NH_3 first global analytical PES from *ab initio* that (nearly) fulfills expectations regarding both spectroscopy and reaction dynamics .

CO/Cu(100) first global analytical PES from *ab initio*. Diffusion barrier agrees well with experimental value after inclusion of zero point energy. Cluster type models insufficient for lateral potentials!