Vibrational Levels Associated with Hydrogen Bonds *

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* Joint work with

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Setup

Tri-atomic molecule

- Nuclei A, B, C
  molecular Hamiltonian

$$-\frac{1}{2m_A}\Delta_{x_A} - \frac{1}{2m_B}\Delta_{x_B} - \frac{1}{2m_C}\Delta_{x_C} + h_e(x_A, x_B, x_C)$$

with $h_e(x_A, x_B, x_C)$ the electronic Hamiltonian

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- Jacobi Coordinates
  R total C.M., x_{AB} C.M. of A and B
  $W = x_B - x_A$, $Z = x_C - x_{AB}$
  $\Rightarrow$ M total mass, $m_{AB} = m_A + m_B$,

$$-\frac{1}{2M}\Delta_R - \frac{m_{AB}}{2m_A m_B}\Delta_W - \frac{M}{2m_{AB}m_C}\Delta_Z + h_e(W, Z)$$

Bond states only $\Rightarrow$ discard the K.E. $-\frac{1}{2M}\Delta_R$ of the C.M.

Born-Oppenheimer Approximation

Scaling

- $m_{elec.} = 1\,,\ M_{nuc.} = \epsilon^{-4}$

Ground state

- $E_{GS}(W, Z)$, G.S. electronic surface of $h_e(W, Z)$, s.t.

$$E_{G.S}(W, Z) \simeq E_0 + q_1(W - W_0)^2 + q_2(Z - Z_0)^2 + \cdots$$

Born-Oppenheimer Approximation '27

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Harmonic approximation

- $-\frac{\epsilon^4}{2}\,\Delta_W - \frac{\epsilon^4}{2}\,\Delta_Z + \sum_j \frac{\omega_j(1)^2}{2}(W-W_0)_j^2 + \frac{\omega_j(2)^2}{2}(Z-Z_0)_j^2$

Vibrational levels

- $\mathcal{E}(\epsilon) = E_0 + \epsilon^2(\sum_j \omega_j(1)(n_j+\frac{1}{2}) + \omega_j(2)(m_j+\frac{1}{2})) + O(\epsilon^4)$

Landmarks '75-'90

Combes-Duclos-Seiler, Hagedorn, Hunziker, Klein-Martinez-Seiler-Wang, ...

B-O vs. H-Bonds

If an Hydrogen is involved in H-bond

- H nucleus less bound than typical nucleus
- $M_H \simeq$ 10 times smaller than typical $M_{nucl.}$
- Vibrational levels are more “anharmonic”
- Experimental and numerical data still under discussion

  e.g. Kawaguchi-Hirota ’87, Elghobashi-Gonzalez ’06

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Modification of B-O in two cases

Symmetric linear molecule

Non-symmetric tri-dimensional molecule

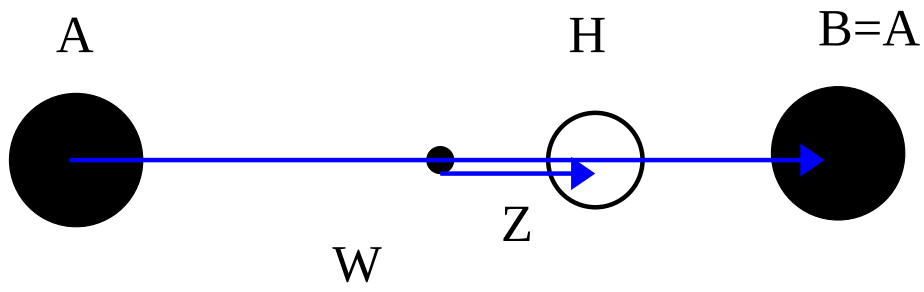
with

- Different mass scales
- Adapted Model of G.S. electronic surface
- Motivated by numerics on the ion FHF^- and $FHCl^-$

Symmetric case

Modification of B-O in simplified setting

- Linear molecule $\Rightarrow$ no rotation, no bending



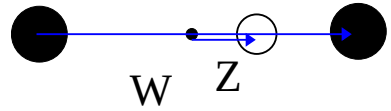
- Different mass scaling $A \equiv B$ heavier than H :

$$M_A = M_B = \epsilon^{-4}, M_H = \epsilon^{-3}$$

With $\epsilon \simeq 0.082 \leftrightarrow$ Carbon, $M_H = 1.015\, \epsilon^{-3}$

- ϵ-dependent G.S. electronic surface s.t. H less bound than A, B

The model



Symmetric case

- Numerics on the G.S. of FHF^- suggest

$$E_{GS}(\epsilon, W, Z) = E_0 + a_1(W - W_0)^2 + (a_2\epsilon - a_3(W - W_0))Z^2 + a_4 Z^4 + \cdots ,$$

$$\equiv E_1(\epsilon, W, Z) + O((W - W_0)^\alpha Z^{2\beta}), \quad \alpha, \beta \in \mathbb{N}, \ \ \alpha + \beta \geq 3$$

with $a_j = O(1)$ and $\epsilon \leftrightarrow$ Carbon.

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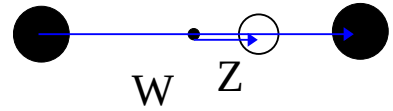

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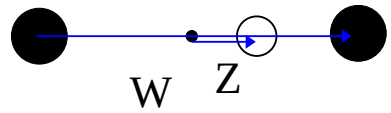
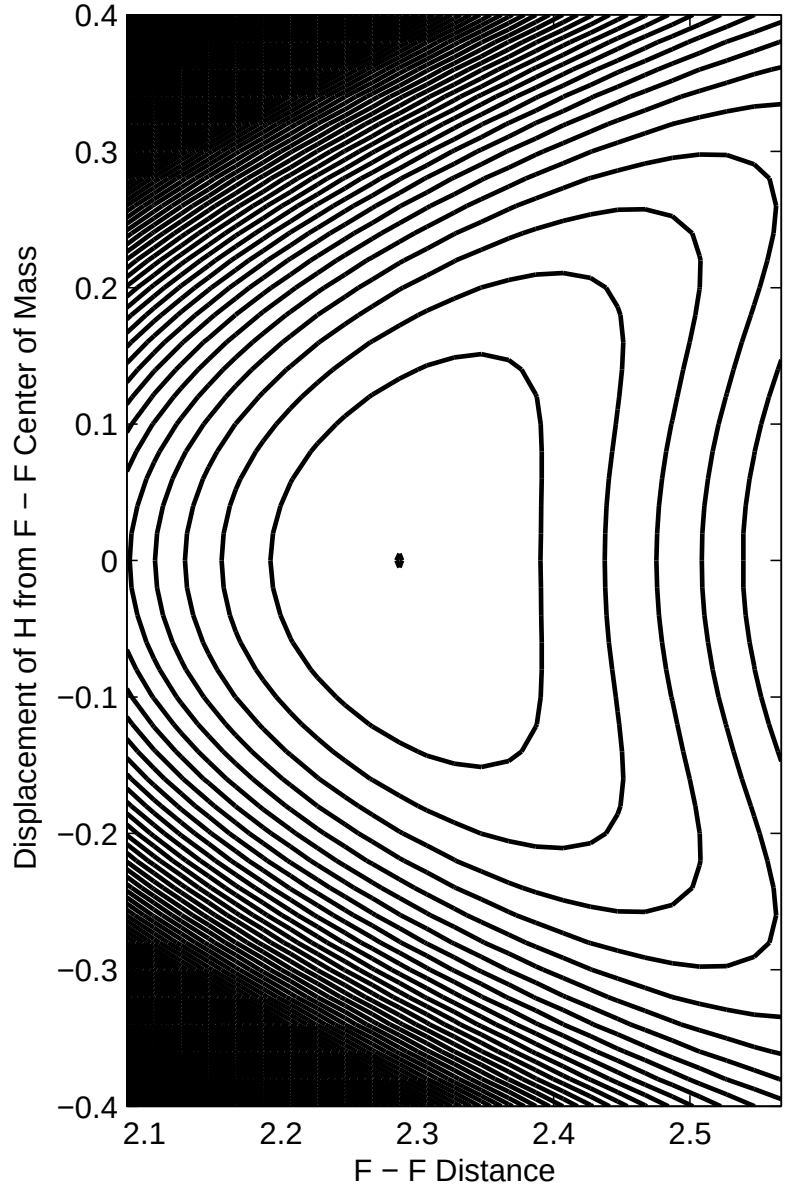
Condition $a_1, a_3, a_4 > 0$ and

$$\left.\begin{array}{ll} \text{either} & a_3^2 < 4a_1a_4 \\ \text{or} & a_3^2 = 4a_1a_4 \end{array} \quad \text{and} \quad a_2 \geq 0 \right\} \Leftrightarrow \quad E_1(\epsilon, W, Z) \geq -C$$

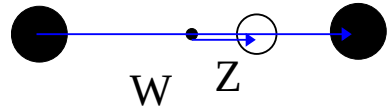
The model



Typically



The model



Leads to the scalar Hamiltonian (up to constants)

$$H_S(\epsilon) = -\frac{\epsilon^4}{2}\frac{\partial^2}{\partial W^2} - \frac{\epsilon^3}{2}\frac{\partial^2}{\partial Z^2} + E_1(\epsilon, W, Z)$$

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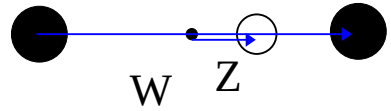

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Rescaling

With $w = (W - W_0)/\epsilon$ and $z = Z/\epsilon^{1/2}$,
$H_S(\epsilon)$ equivalent to $E_0 + \epsilon^2 H_{NF}$ where

$$H_{NF} = -\frac{1}{2}\frac{\partial^2}{\partial w^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} + E_{NF}(w, z), \quad \text{where}$$

$$E_{NF}(w, z) = a_1 w^2 + (a_2 - a_3 w)z^2 + a_4 z^4 \geq -C$$

H_{NF} replaces the harm. osc.

Heuristics

Provided

- electronic transitions are small
- physical value of $\epsilon \simeq 0.0821$ is “small enough”
- fitting of G.S. electronic surface yields suitable parameters
- higher order corrections in $E_{GS}(\epsilon, W, Z)$ are negligeable
- H_{NF} has discrete spectrum

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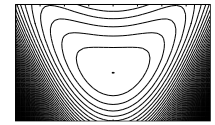
First vibrational levels

$$\mathcal{E}(\epsilon) \simeq E_0 + \epsilon^2 \mathcal{E}_2,$$

where $\mathcal{E}_2 \in \sigma_d(H_{NF})$.



Numerics

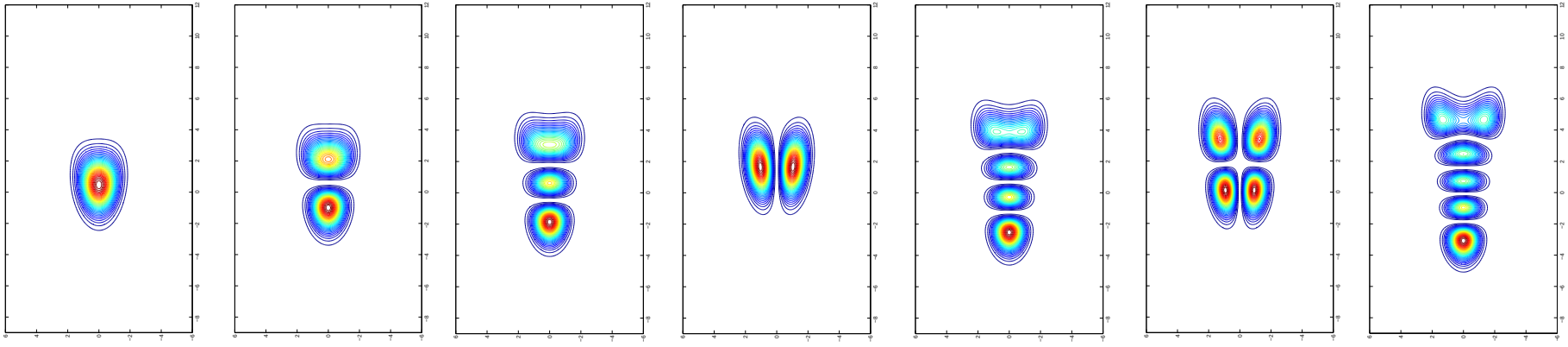
Comparison with experimental data for FHF^-

$[L]$ = Angstroms, $[E]$ = Hartrees, and $\epsilon = 0.0821$.

- Fitting yields

$$W_0 = 2.287, E_0 = -200.215, a_1 = 0.26, a_2 = 1.22, a_3 = 1.29, a_4 = 1.62,$$

- Experiment: first sym., antisym. and sym+asym. streching modes are
  583.05 cm $^{-1}$, 1331.15 cm $^{-1}$, and 1849 cm $^{-1}$
- Predictions from the model are
  600 cm $^{-1}$, 1399 cm $^{-1}$, and 1942 cm $^{-1}$.



Mathematical method

Spectral problem

Find $\mathcal{E}(\epsilon)$ and $\Psi(\epsilon, W, Z)$ s.t.

$$H_{mol}(\epsilon)\Psi(\epsilon, W, Z) = \mathcal{E}(\epsilon)\Psi(\epsilon, W, Z)$$

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Multiscale analysis

Look for quasimodes of the form

$$\Psi(\epsilon, W, Z) = \psi(\epsilon, W, Z, w, z)|_{w=W/\epsilon, z=Z/\sqrt{\epsilon}}$$

where (W, Z) is the electronic scale and (w, z) is the nuclear scale.

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Ansatz

- $\mathcal{E}(\epsilon) = \mathcal{E}_0 + \epsilon^{1/2}\mathcal{E}_{1/2} + \epsilon^1\mathcal{E}_1 + \dots$
- $\psi(\epsilon, W, Z, w, z) = \psi_0(W, Z, w, z) + \epsilon^{1/2}\psi_{1/2}(W, Z, w, z) + \cdots$

Expansion

$$\mathcal{E}(\epsilon) \in \sigma(-\tfrac{\epsilon^4}{2}\tfrac{\partial^2}{\partial W^2} - \tfrac{\epsilon^3}{2}\tfrac{\partial^2}{\partial Z^2} + h_e(\epsilon, W, Z))$$

Theorem CMP '07

Under reasonable assumptions, as $\epsilon \to 0$,

$$\begin{aligned} \mathcal{E}(\epsilon) &\simeq \sum_{j=0}^{\infty} \epsilon^{j/2} \mathcal{E}_{j/2} \\ &= E_0 + \epsilon^2 \mathcal{E}_2 + O(\epsilon^{5/2}), \end{aligned}$$

where $\mathcal{E}_2 \in \sigma_d(H_{NF})$.

$$\Psi_Q(\epsilon, W, Z) \simeq \sum_{j=0}^{\infty} \epsilon^{j/2} \psi_{j/2}(W, Z, W/\epsilon, Z/\sqrt{\epsilon}),$$

modulo cutoff function.

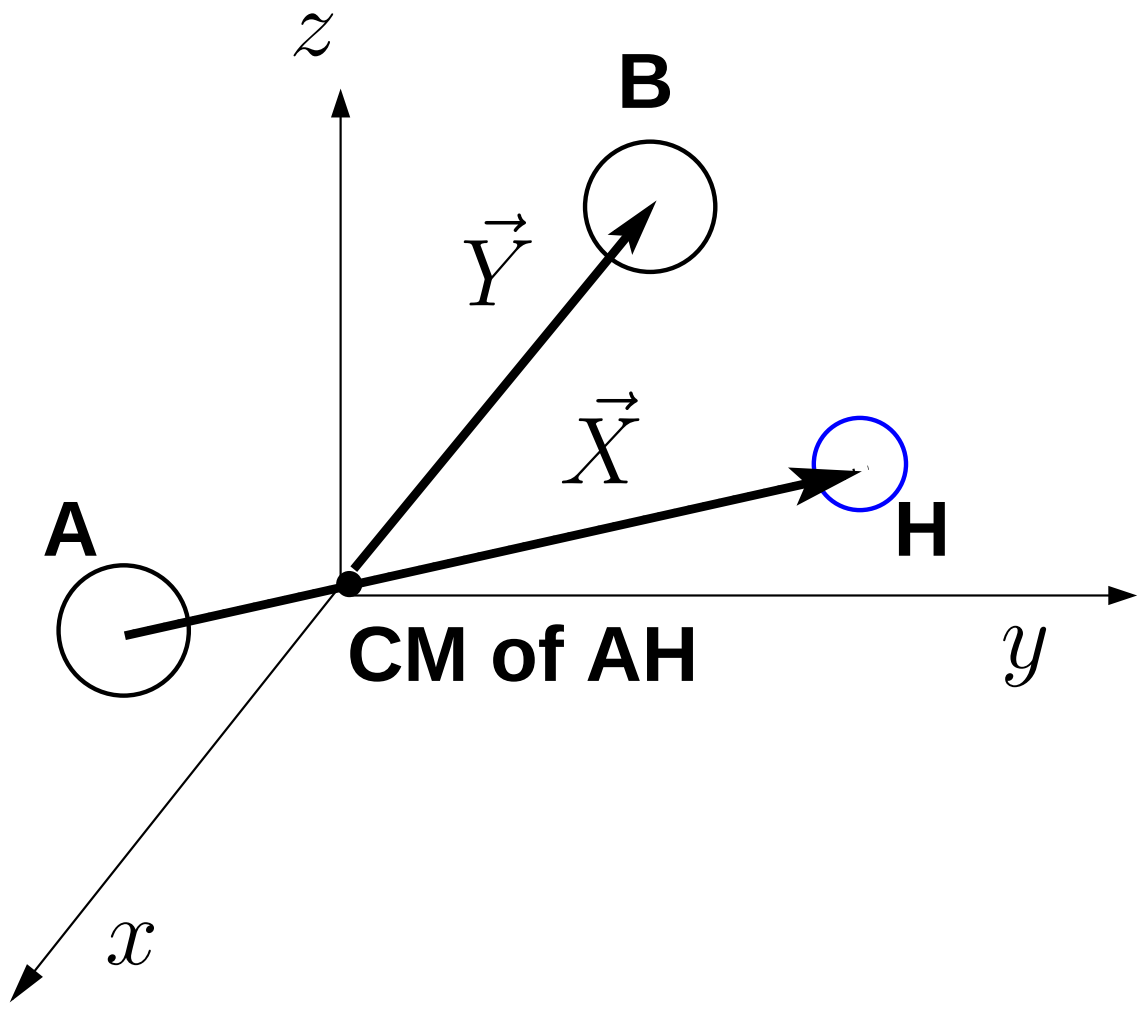
Proof

- plug in the Ansatz and equate like powers of $\epsilon^{1/2}$.

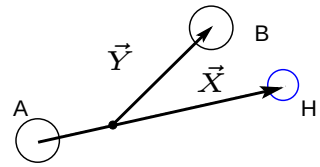
Non-symmetric case

Modification of B-O in simplified setting

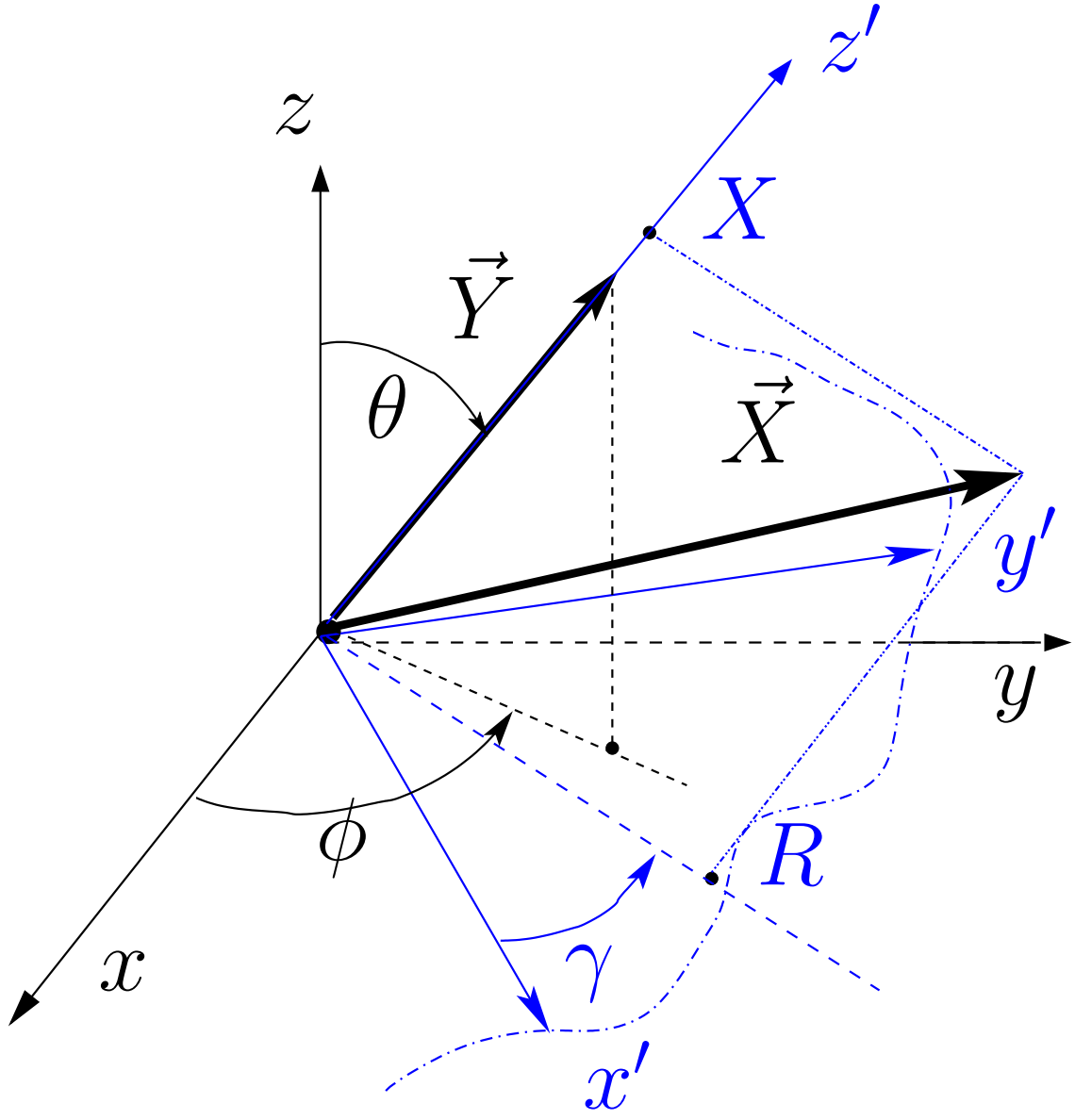
- Full 3-D molecule $\Rightarrow$ rotation and bending included



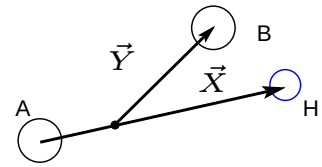
Variables



- Spherical $\vec{Y} = (Y, \theta, \phi)$ and Cyclindrical $\vec{X} = (R, \gamma, X)$ variables



Modification of B-O



Model

- ϵ-dependent G.S. electronic surface s.t.

$AHB \simeq AH + B$ and linear equilibrium:

$$E_{GS}(\epsilon, X, R, Y) = V_1(X) + \epsilon V_2(X, R, Y)$$

$$\begin{aligned} V_1(X) &\simeq a_0 + a_2(X - X_0)^2 + a_3(X - X_0)^3 + \cdots \\ V_2(X, R, Y) &\simeq b_{0,2,0}R^2 + b_{1,0,1}(X - X_0)(Y - Y_0) + b_{0,0,2}(Y - Y_0)^2 + \cdots \end{aligned}$$

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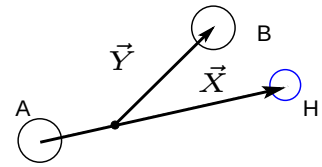

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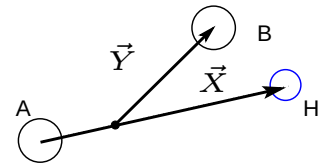
$$M_A = m_A\epsilon^{-4}, M_B = m_B\epsilon^{-4}, M_H = m_H\epsilon^{-3}$$

With $\epsilon \simeq 0.082 \leftrightarrow$ Carbon, $M_H = 1.015\ \epsilon^{-3}$

Heuristics



Reduced scalar problem

$$H_S = -\frac{\epsilon^3}{2\mu_1(\epsilon)}\Delta_{\vec{X}} - \frac{\epsilon^4}{2\mu_2(\epsilon)}\Delta_{\vec{Y}} + V_1(X) + \epsilon V_2(X, R, Y)$$

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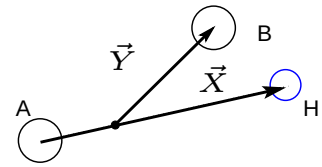

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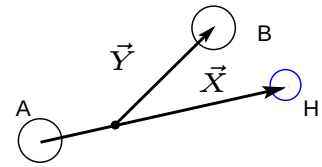
with $\mu_j(\epsilon) = \mu_j + o(1)$, and J^2, $L\cdot J$ and L^2 messy op's involving angles.

Heuristics



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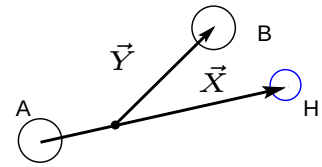
Leading order: $Y \simeq Y_0$, $X \simeq X_0$

$$\begin{aligned} H_S &\simeq a_0 - \frac{\epsilon^3}{2\mu_1}\left(\frac{\partial^2}{\partial R^2} + \frac{1}{R}\frac{\partial}{\partial R} + \frac{1}{R^2}\frac{\partial^2}{\partial \gamma^2}\right) + \epsilon b_{0,2,0}R^2 \\ &- \frac{\epsilon^3}{2\mu_1}\frac{\partial^2}{\partial X^2} + a_2(X-X_0)^2 - \frac{\epsilon^4}{2\,\mu_2}\frac{\partial^2}{\partial Y^2} + \epsilon b_{0,0,2}(Y-Y_0)^2 \\ &+ \epsilon b_{1,0,1}(X-X_0)(Y-Y_0) + \cdots \end{aligned}$$

Heuristics



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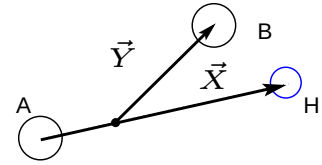
$\leftarrow$ Higher Order

Leading orders



Heuristically

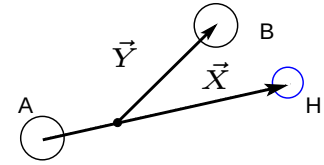
$H_S \simeq$ 3 indep. harm. oscil. with

$$\mathcal{E}_X(\epsilon) = \epsilon^{3/2}\sqrt{2a_2/\mu_1}(n_1+1/2) \qquad A-H \text{ oscillat. modes}$$

$$\mathcal{E}_{R,\gamma}(\epsilon) = \epsilon^{4/2}\sqrt{2b_{0,2,0}/\mu_1}(n_2+1) \qquad \text{2 degenerate bending modes}$$

$$\mathcal{E}_Y(\epsilon) = \epsilon^{5/2}\sqrt{2b_{0,0,2}/\mu_2}(n_3+1/2) \qquad AH-B \text{ oscillat. modes}$$

Leading orders



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$H_S \simeq$ 3 indep. harm. oscil. with

$$\mathcal{E}_X(\epsilon) = \epsilon^{3/2}\sqrt{2a_2/\mu_1}(n_1+1/2) \qquad A-H \text{ oscillat. modes}$$

$$\mathcal{E}_{R,\gamma}(\epsilon) = \epsilon^{4/2}\sqrt{2b_{0,2,0}/\mu_1}(n_2+1) \qquad \text{2 degenerate bending modes}$$

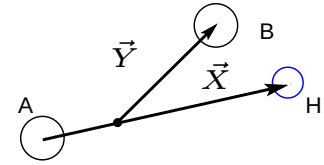
$$\mathcal{E}_Y(\epsilon) = \epsilon^{5/2}\sqrt{2b_{0,0,2}/\mu_2}(n_3+1/2) \qquad AH-B \text{ oscillat. modes}$$

Comparisons for $FHCl^-$ $[L]$ = Angstroms, $[E]$ = Hartrees, and $\epsilon = 0.0821$.

- Fitting

  $a_0 = -560.160$, $a_2 = 0.567$, $b_{0,2,0} = 0.597$, $b_{1,0,1} = 0.853$, $b_{0,0,2} = 0.664$

Leading orders



Heuristically

$H_S \simeq$ 3 indep. harm. oscil. with

$$\mathcal{E}_X(\epsilon) = \epsilon^{3/2}\sqrt{2a_2/\mu_1}(n_1+1/2) \qquad A-H \text{ oscillat. modes}$$

$$\mathcal{E}_{R,\gamma}(\epsilon) = \epsilon^{4/2}\sqrt{2b_{0,2,0}/\mu_1}(n_2+1) \qquad \text{2 degenerate bending modes}$$

$$\mathcal{E}_Y(\epsilon) = \epsilon^{5/2}\sqrt{2b_{0,0,2}/\mu_2}(n_3+1/2) \qquad AH-B \text{ oscillat. modes}$$

Comparisons for $FHCl^-$ $[L]$ = Angstroms, $[E]$ = Hartrees, and $\epsilon = 0.0821$.

- Fitting

  $a_0 = -560.160,\ a_2 = 0.567,\ b_{0,2,0} = 0.597,\ b_{1,0,1} = 0.853,\ b_{0,0,2} = 0.664$

- unit: cm $^{-1}$

Mode	Experiment*	Gaussian '03	Our Model
$F-H$ stretch	2710	2960	2960
bends (degenerate)	843	875	871
$FH-Cl$ stretch	275	246	251

* Evans & Lo '66

Multiscale analysis

RMP 09

- Introduce rescaled variables
  $y = (Y - Y_0)/\epsilon^{3/4}$, $r = R/\epsilon^{1/2}$, $x = (X - X_0)/\epsilon^{3/4}$,
- Scalar Hamiltonian

  $H_S(\epsilon)\Psi(\epsilon) = \mathcal{E}(\epsilon)\Psi(\epsilon)$ has asymptotic solutions

$$\begin{aligned}
\Psi(\epsilon) &\simeq \sum_j \epsilon^{j/4} \psi_{j/4}(Y, R, X, y, r, x, \theta, \phi, \gamma)\big|_{y=\frac{Y-Y_0}{\epsilon^{3/4}}, r=\frac{R}{\epsilon^{1/2}}, x=\frac{X-X_0}{\epsilon^{3/4}}} \\
\mathcal{E}(\epsilon) &\simeq \sum_j \epsilon^{j/4} \mathcal{E}_{j/4} \\
&= \mathcal{E}_X(\epsilon) + \mathcal{E}_{R,\gamma}(\epsilon) + \mathcal{E}_Y(\epsilon) + O(\epsilon^3)
\end{aligned}$$

Inclusion of electrons

- Molecular Hamiltonian

$$\mathcal{E}(\epsilon) = \mathcal{E}_X(\epsilon) + \mathcal{E}_{R,\gamma}(\epsilon) + \mathcal{E}_Y(\epsilon) + O(\epsilon^3)$$

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