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# Vibrational Levels Associated with Hydrogen Bonds\*

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\* Joint work with



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# Setup

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## 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.

## 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.

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

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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

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

## Landmarks '75-'90

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

# B-O vs. H-Bonds

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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

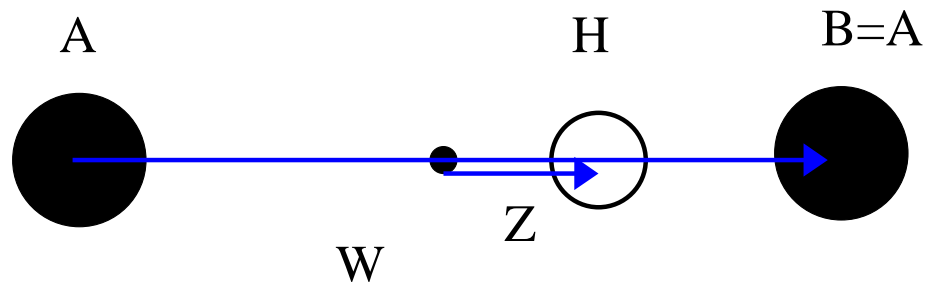
with

- 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  $H$ :

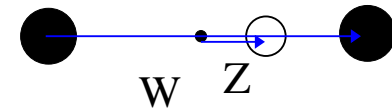
$$M_A = M_B = \epsilon^{-4}, M_H = \epsilon^{-3}$$

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

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



# The model



## Symmetric case

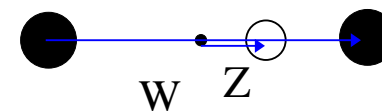
- Numerics on the G.S. of  $FHF^-$  suggest

$$E_{GS}(\epsilon, W, Z) = E_0 + a_1(W - W_0)^2 + (a_2\epsilon - a_3(W - W_0))Z^2 + a_4Z^4 + \dots,$$

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

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

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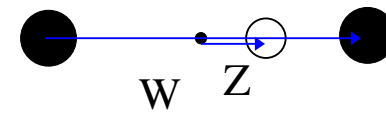
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## Condition

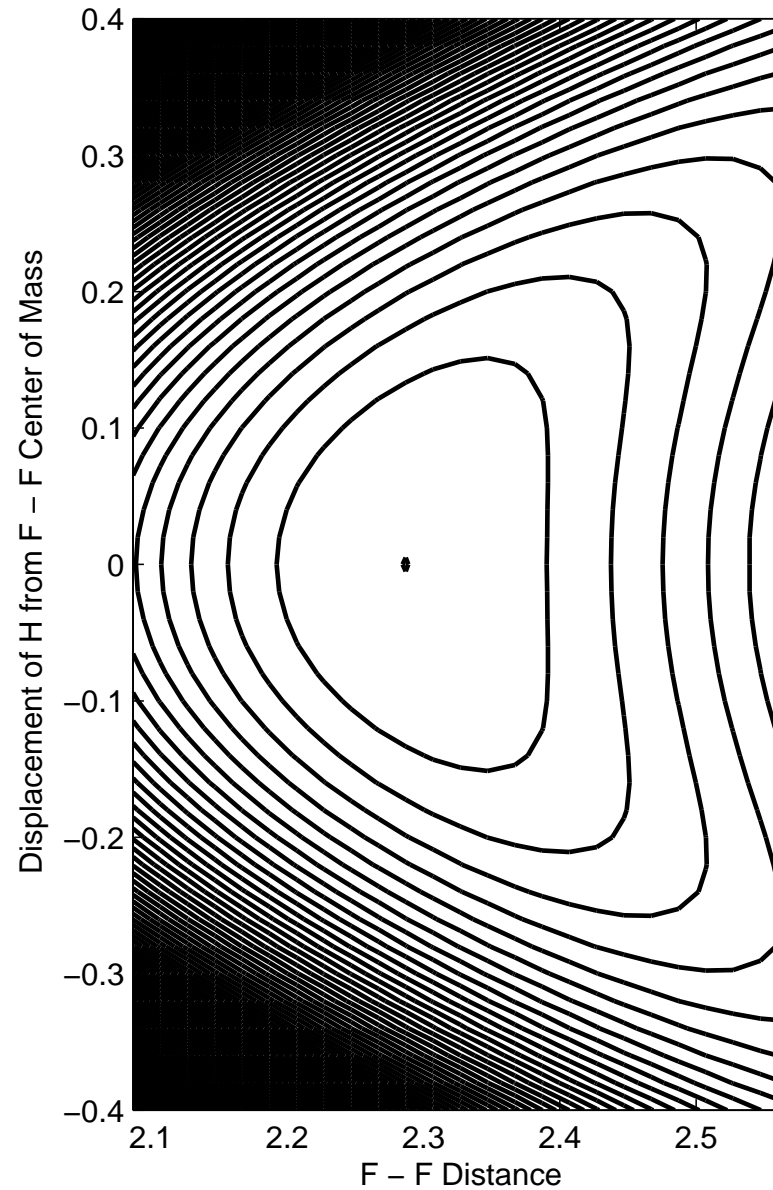
$$a_1, a_3, a_4 > 0 \text{ and}$$

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

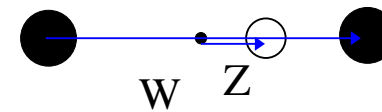
# The model



Typically



# The model

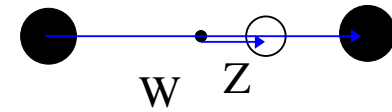


Leads to the scalar Hamiltonian

(up to constants)

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

# The model



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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

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

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

$H_{NF}$  replaces the harm. osc.

# Heuristics

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## 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 negligible
- $H_{NF}$  has discrete spectrum

# Heuristics

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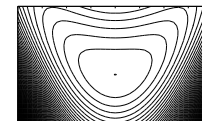
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## First vibrational levels

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

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



# Numerics

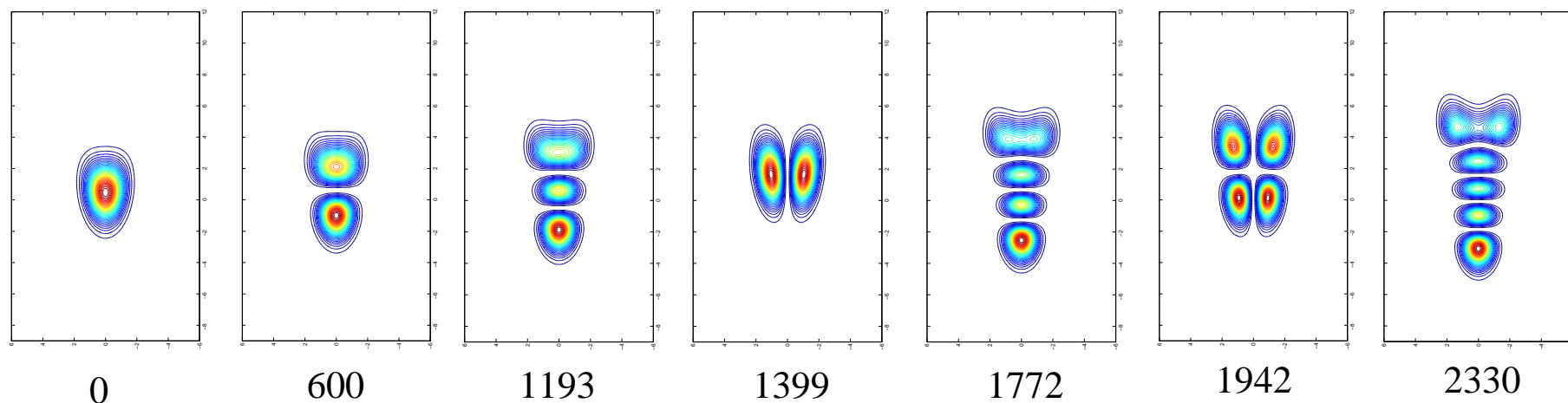
Comparison with experimental data for  $FHF^-$

$[L] = \text{Angstroms}$ ,  $[E] = \text{Hartrees}$ , 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. stretching modes are  $583.05 \text{ cm}^{-1}$ ,  $1331.15 \text{ cm}^{-1}$ , and  $1849 \text{ cm}^{-1}$
- **Predictions** from the model are  $600 \text{ cm}^{-1}$ ,  $1399 \text{ cm}^{-1}$ , and  $1942 \text{ cm}^{-1}$ .





# Mathematical method

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## 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

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

# Expansion

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

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## Theorem

CMP '07

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

$$\begin{aligned}\mathcal{E}(\epsilon) &\simeq \sum_{j=0}^{\infty} \epsilon^{j/2} \mathcal{E}_{j/2} \\ &= E_0 + \epsilon^2 \mathcal{E}_2 + O(\epsilon^{3/2}),\end{aligned}$$

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.

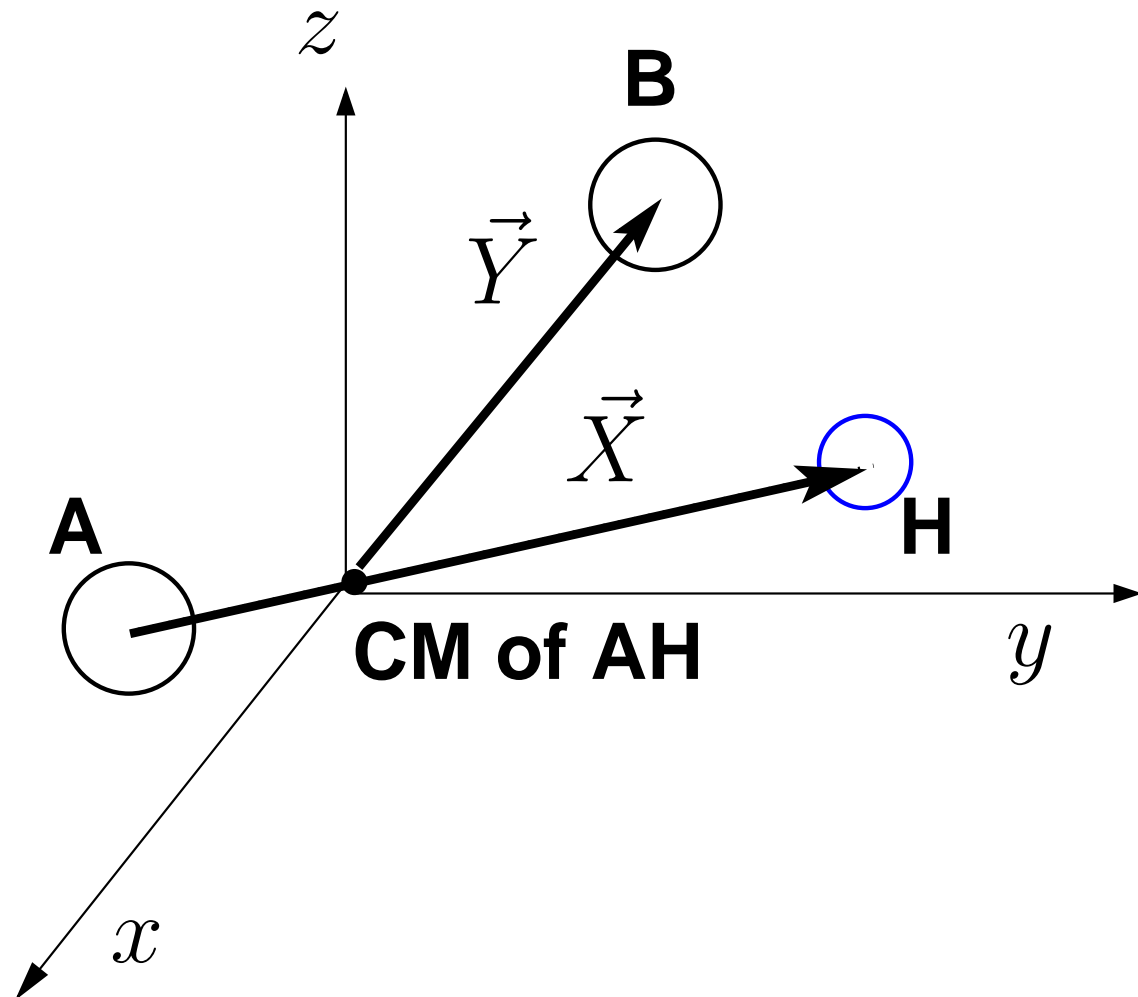
## Proof

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

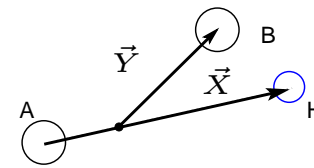
# Non-symmetric case

## Modification of B-O in simplified setting

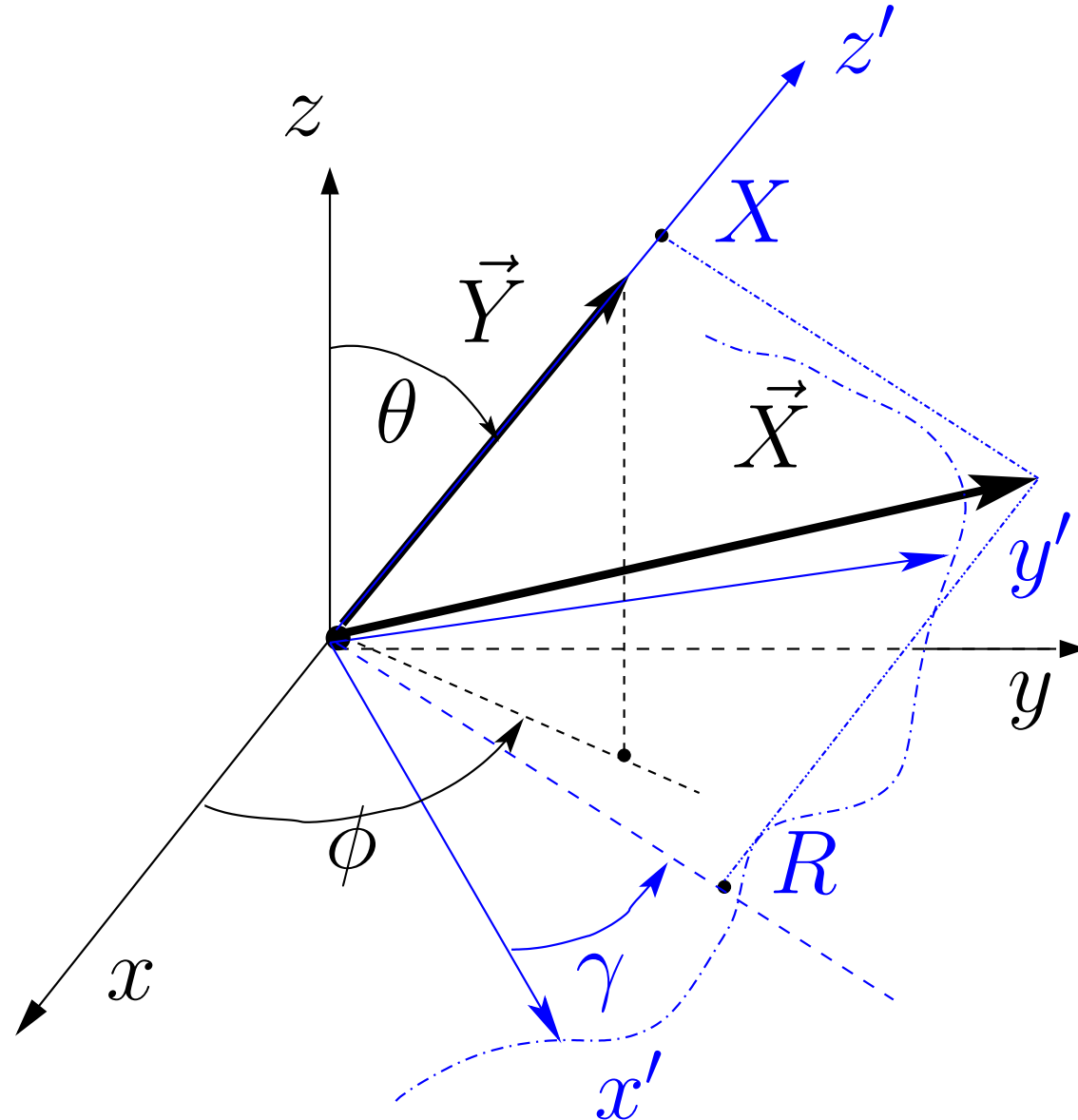
- Full 3-D molecule  $\Rightarrow$  rotation and bending included



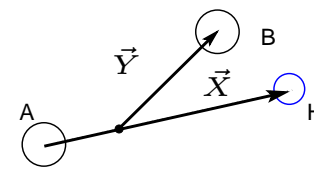
# Variables



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



# Modification of B-O



## Model

- $\epsilon$ -dependent G.S. electronic surface s.t.

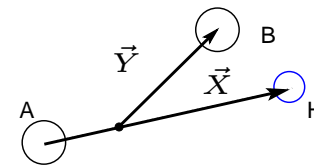
$AHB \simeq AH + B$  and linear equilibrium:

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

$$V_1(X) \simeq a_0 + a_2(X - X_0)^2 + a_3(X - X_0)^3 + \dots$$

$$V_2(X, R, Y) \simeq b_{0,2,0}R^2 + b_{1,0,1}(X - X_0)(Y - Y_0) + b_{0,0,2}(Y - Y_0)^2 + \dots$$

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- Mass scaling  $A \neq B$  heavier than  $H$ :

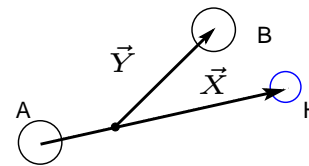
$$M_A = m_A \epsilon^{-4}, M_B = m_B \epsilon^{-4}, M_H = m_H \epsilon^{-3}$$

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# Heuristics

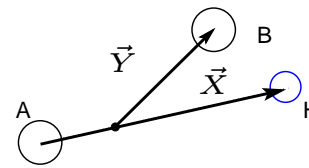
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Reduced scalar problem

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

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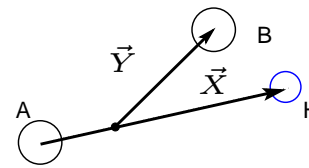


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 &\quad - \frac{\epsilon^4}{2\mu_2(\epsilon)} \left( \frac{\partial^2}{\partial Y^2} + \frac{2}{Y} \frac{\partial}{\partial Y} - \frac{1}{Y^2} \{ J^2 - 2L \cdot J + L^2 \} \right) \\
 &\quad + V_1(X) + \epsilon V_2(X, R, Y)
 \end{aligned}$$

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

# Heuristics



## Reduced scalar problem

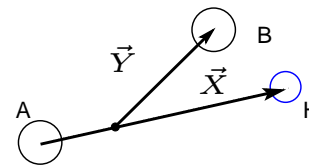
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Leading order:  $Y \simeq Y_0$ ,  $X \simeq X_0$

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# Heuristics



## Reduced scalar problem

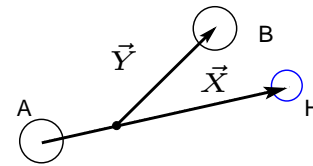
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 &\quad + \epsilon b_{1,0,1} \cancel{(X - X_0)} (Y - Y_0) + \dots \quad \leftarrow \text{Higher Order}
 \end{aligned}$$

# Leading orders



Heuristically

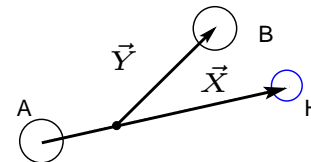
$H_S \simeq 3$  indep. harm. oscil. with

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

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

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

# Leading orders



Heuristically

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

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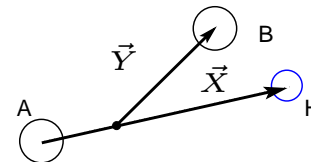
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Comparisons for  $FHCl^-$   $[L] =$  Angstroms,  $[E] =$  Hartrees, and  $\epsilon = 0.0821$ .

- Fitting

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

# Leading orders



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

- Fitting

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

- unit:  $\text{cm}^{-1}$

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

Preprint '08

- Introduce rescaled variables

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

- Scalar Hamiltonian

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

$$\Psi(\epsilon) \simeq \sum_j \epsilon^{j/4} \psi_{j/4}(Y, R, X, y, r, x, \theta, \phi, \gamma) \Big|_{y=\frac{Y-Y_0}{\epsilon^{3/4}}, r=\frac{R}{\epsilon^{1/2}}, x=\frac{X-X_0}{\epsilon^{3/4}}}$$

$$\mathcal{E}(\epsilon) \simeq \sum_j \epsilon^{j/4} \mathcal{E}_{j/4}$$

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

## Inclusion of electrons

- Molecular Hamiltonian

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