Mathematical models and some challenges in Quantum chemistry

G. Friesecke, TU Munich http://www-m7.ma.tum.de

Tutorial

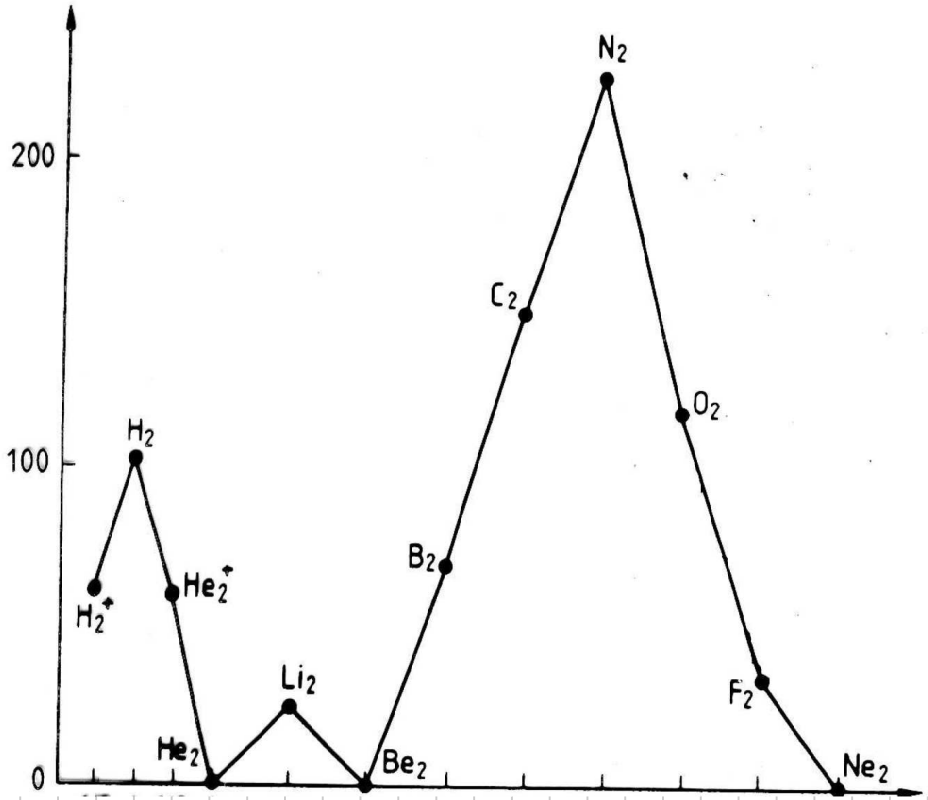
Workshop 'Density Functional theory: Fundamentals and Applications in Condensed Matter Physics',
Organizers: E. Cancès, C. J. Garcia-Cervera, Y. A. Wang

Banff, 24.1.2011

0. Chemical facts
1. Many-body Schrödinger eq.
2. Approx's & reduced models
3. Some challenges.

0. Chemical facts.

a) Binding energies and molecular geometries depend spectacularly on type of atom.



Experimental binding energies, homonuclear dimers

H_2O

Li_2O

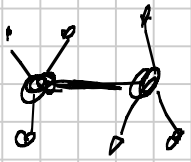
Experimental geometries. Note H & Li are even in same group!

b) Binding en. of a particular bond depends spectacularly on chem. environment.

$H_3C - CH_3$ 83 $\frac{kcal}{mol}$

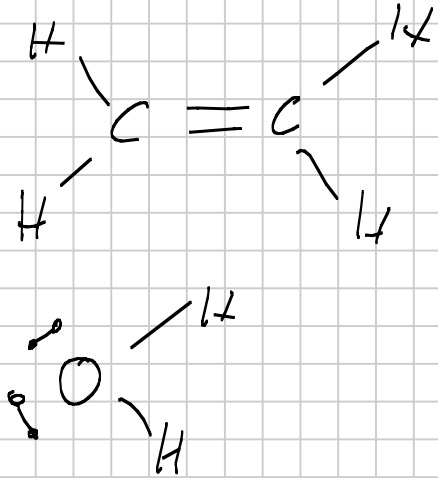
$H_2C - CH_2$ 125

$HC - CH$ 230



Semi-empirical/semi-quantum mechanical models explain some trends, but are not quantitative

- Lewis structure (1916)
- molecular orbital theory (+ Hund's rule)
- VSEPR (1940)
  (valence-shell electron pair repulsion)



Goal of Quantum chemistry

predict data as close accurately & ab initio (ie from a QM model whose only input are atomic no's), for complex molecules.

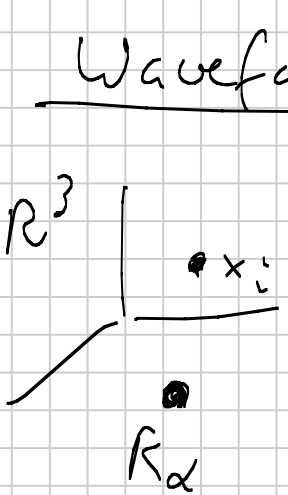
1. Many-body Schrödinger eq.

Input: N ... #el's

$z_1, \dots, z_M$ ... charges of nuclei (usually $\sum z_\alpha = N$)

$m_1, \dots, m_M$ ... masses —//—

Wavefctn of system:



$$\Psi \in L^2\left((\mathbb{R}^3 \times \mathbb{Z}_2)^N \times (\mathbb{R}^3)^M\right)$$

$$\Psi = \Psi(x_1, s_1, \dots, x_N, s_N; R_1, \dots, R_M)$$

$x_i \in \mathbb{R}^3$ position coord. i^{th} el., $R_\alpha \in \mathbb{R}^3$ pos. coord. α^{th} nucleus, $s_i \leftrightarrow$ el. spins

Antisymmetric under exchange $(x_i, s_i) \leftrightarrow (x_j, s_j)$

Symm. or antisymm. —//— identical nuclei

Schröd. eq.:

(1) $$\boxed{i\partial_t \Psi = H\Psi}$$

$$H = T_n + T_e + V_{ne} + V_{ee} + V_{nn}$$

$$T_n = \sum_{\alpha=1}^{M} -\frac{1}{2m_\alpha}\Delta_{R_\alpha}$$

$$T_e = \sum_{i=1}^{N} -\frac{1}{2}\Delta_{x_i}$$

$$V_{ne} = \sum_{i=1}^{N} \underbrace{\left(\sum_{\alpha=1}^{M} \frac{-Z_\alpha}{|x_i - R_\alpha|} \right)}_{=: V_{ne}(x_i)}$$

$$V_{ee} = \sum_{i<j} \frac{1}{|x_i - x_j|}$$

$$V_{nn} = \sum_{\alpha<\beta} \frac{Z_\alpha Z_\beta}{|R_\alpha - R_\beta|}$$

(atomic units $\hbar = |e| = m_e = 4\pi\varepsilon_0 = 1$)

Born-Oppenheimer approximation

$m_\alpha \gg m_e = 1$ $\quad (2000 \lesssim m_\alpha \lesssim 100\,000)$

Ansatz $\quad \Psi(x,R,t) = \psi_e(x,R)\,\chi(R,t)$

(1) $\Leftarrow$ up to $\mathcal{O}(\frac{1}{m_\alpha^2})$ (2) $\boxed{(T_e + V_{ne} + V_{ee} + V_{nn})\,\psi_e = E_e(R)\,\psi_e}$ ESE

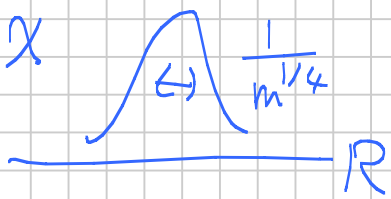
$T_e + V_{ne} + V_{ee} + V_{nn} =: H_e(R)$ electronic Hamiltonian

(3) $\quad i\partial_t \chi = \big(T_n + E_e(R) + \underbrace{a(R) + b(R)}_{\text{error terms}}\big)\chi$

$$a(R) = \int \overline{\psi_e}\, T_n\, \psi_e\, dx = \sum_\alpha \frac{1}{2m_\alpha} \int |\nabla_{R_\alpha} \psi_e|^2 dx = \mathcal{O}\left(\frac{1}{m_\alpha}\right)$$

$$b(R) = -\sum_\alpha \frac{1}{m_\alpha} \int \psi_e\, \nabla_{R_\alpha} \psi_e\, dx \cdot \nabla_{R_\alpha} = \mathcal{O}\left(\frac{1}{m_\alpha^{3/4}}\right)$$

$\uparrow$ on e-states of (3')



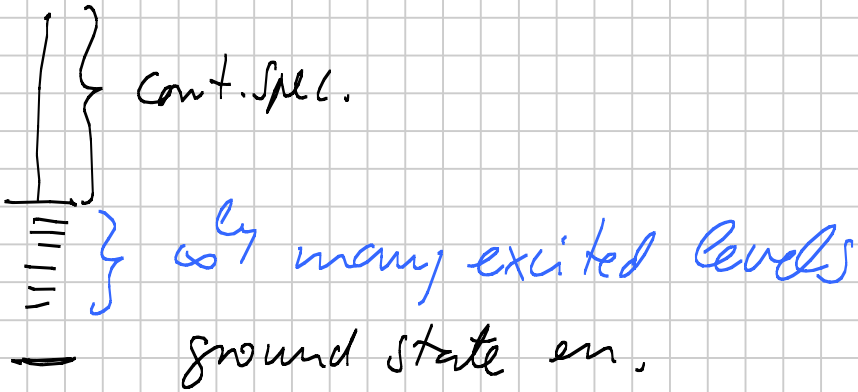
Neglecting a & b ⇝

(3′) $\boxed{i\partial_t \chi = (T_n + E_e(R))\chi}$ NSE

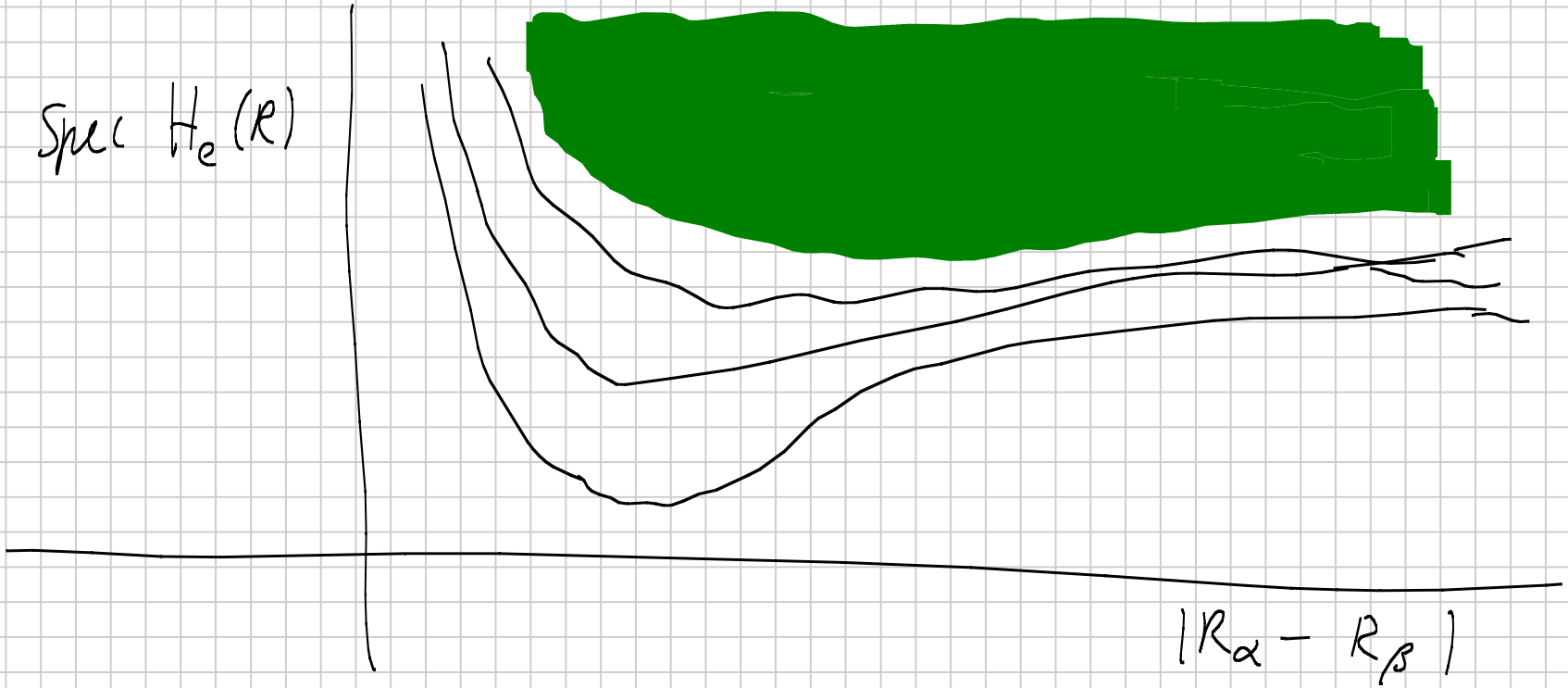
Math. physics community: qualitative theory of (2)

Zhislin's thm: $N \leq Z$ ⇒

spec H_e =



Typical dependence on R:



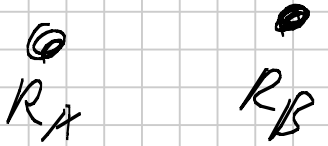
Further approx's of (3) (using $\frac{1}{m} \leq 10^{-3}$)

(3'') $\quad m_\alpha \ddot{R}_\alpha = - \nabla_{R_\alpha} E_e(R)$ $\quad$ molecular dynamics (MD))

(3''') Minimize $E_e(R_1, \ldots R_M)$ geometry optimization
$R_1, \ldots R_M$

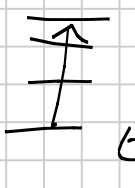
Output: prediction of basic chem. quantities

Bond length $= |R_A^{min} - R_B^{min}|$ (from (3'''))

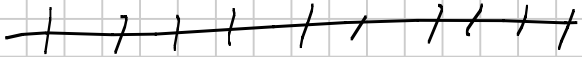


Binding en. $= E_e(R_A^{min}, R_B^{min}, H_{AB})$ (from (2))
$- E_e(H_A) - E_e(H_B)$

Excitation en. $= E_e^{(i)}(R) - E_e^{(j)}(R)$



Problem: curse of dimensionality for (2), (3')

$\mathbb{R}$ $\longrightarrow$ 10 grid points 

$\mathbb{R}^{3N}$ $\longrightarrow$ 10^{3N} —"—

single Carbon atom $\longrightarrow$ 10^{18}

2. Approx's & reduced models