The Calculation of Diffusion Properties for Open Shell Molecules

David W. Schwenke
NASA Ames Research Center
Moffett Field, CA

Sep. 2022

Background:

- Navier-Stokes requires as input various collision integrals for gases
  - Diffusion,
  - Viscosity
  - Thermal conductivity
  - Thermal diffusion ...
- Levin, Stallcop and Partridge state-of-the-art
  - Non-Relativistic Born-Oppenheimer Approximation (freeze nuclei first, let them move second)
  - Solve electron problem: Compute realistic Potential Curves (PC) from first principles,
  - Solve nuclei problem: Compute scattering properties for each PC using sophisticated semi-classical method
  - Compute cross sections
  - Compute appropriate thermal collision integrals

For Mars entry need

- $C+O^+$, $C^+ + O$, $C+O$, $C+C^+$, $C+N^+$, $C^+ + N$
- electron structure calculations for PC
  - MOLPRO fails.
  - need a better tool

For Mars entry need

- $C+O^+$, $C^+ + O$, $C+O$, $C+C^+$, $C+N^+$, $C^+ + N$
- electron structure calculations for PC
  - MOLPRO fails.
  - need a better tool
  - Massively Parallel Electron correlation

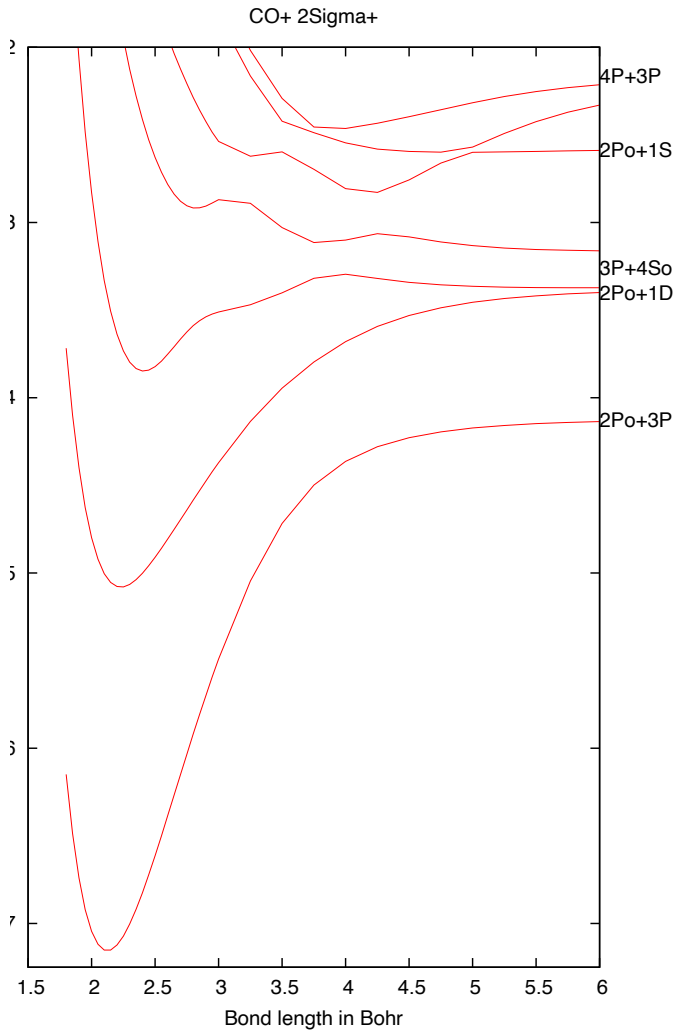
MPEC

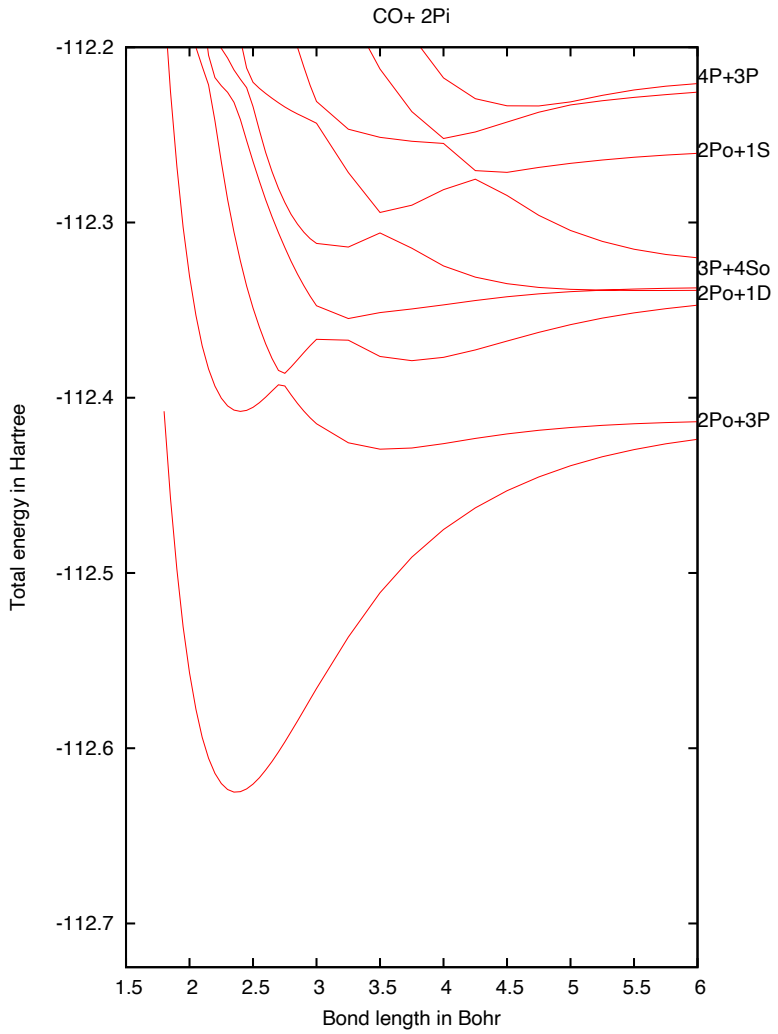
  - MPI parallelization
  - i^2cMRCI
  - full relativistic
  - two-electron matrix elements

CO+

- $C^+ \ ^2P^o$ and O ^3P
  - Σ^+, $2\Sigma^-$, 2Π, Δ; doublet and quartet
- C ^3P and $O^+ \ ^4S^o$
  - Σ^+ and Π; doublet, quartet, and sextet

CO+

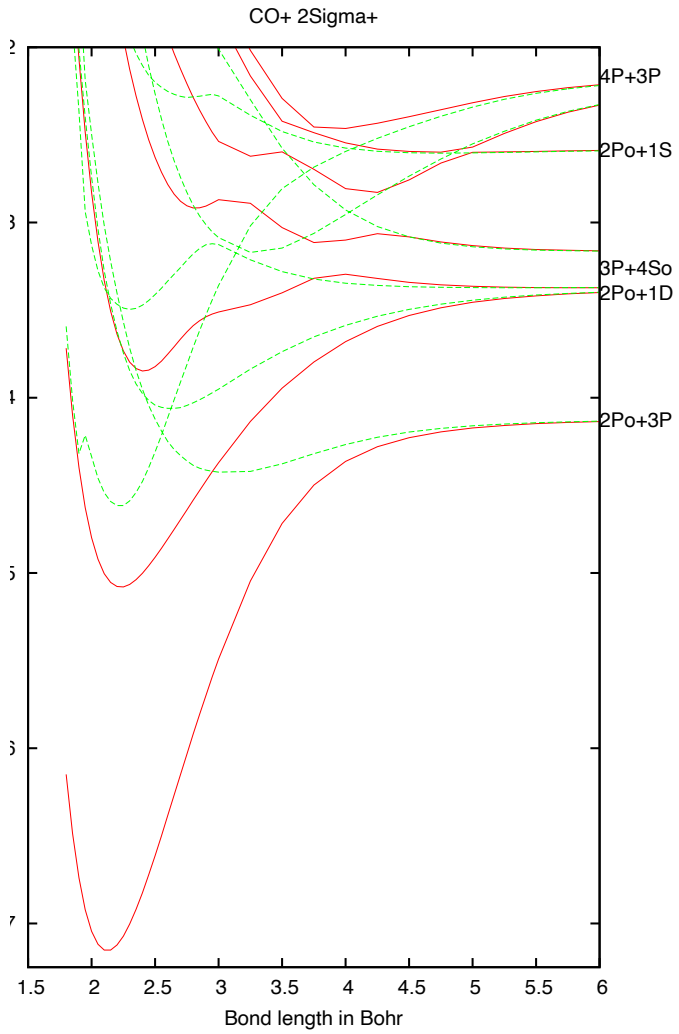

CO+ 2Sigma+
4P+3P
2Po+1S
3P+4So
2Po+1D
2Po+3P
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
Bond length in Bohr

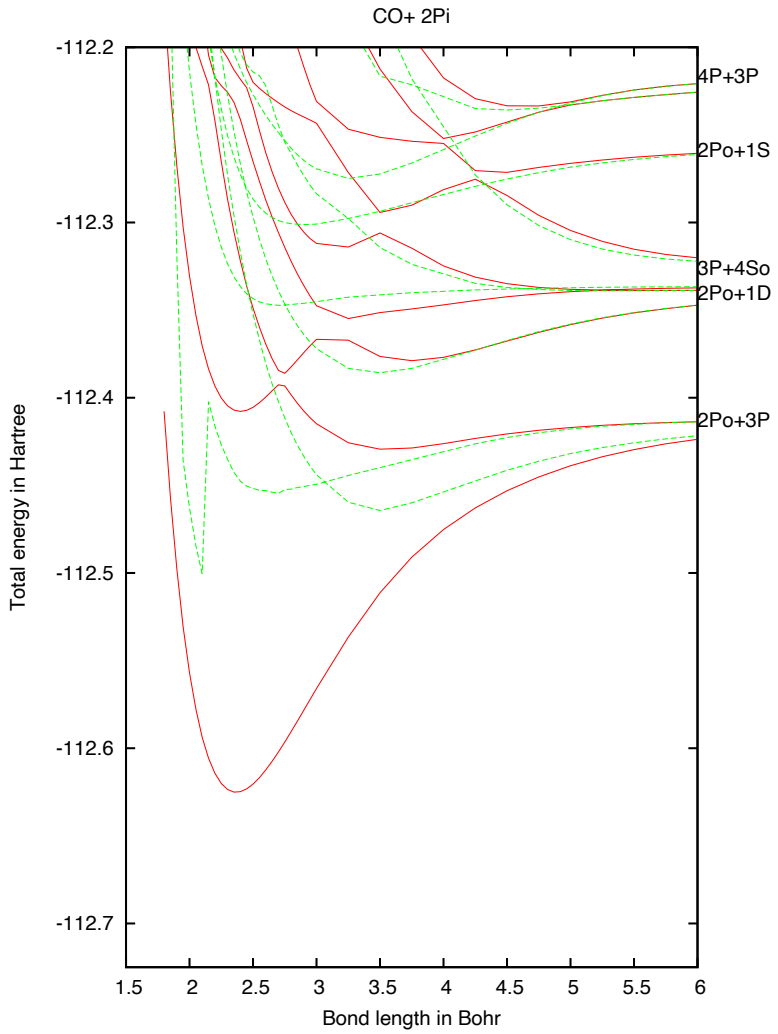

CO+ 2Pi
-112.2
-112.3
-112.4
-112.5
-112.6
-112.7
Total energy in Hartree
4P+3P
2Po+1S
3P+4So
2Po+1D
2Po+3P
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
Bond length in Bohr

Dealing with avoided crossings of adiabatic states

- Hard to interpolate
- "Small" corrections to Born-Oppenheimer approximation no longer small
  - Transform to equivalent electronic basis that is smoother and "small" corrections are small: the diabatic basis
  - Definition fuzzy
  - New method for diabatic basis set
    - Requires coupled states
    - More atomic state thresholds

CO+


CO+ 2Sigma+
4P+3P
2Po+1S
3P+4So
2Po+1D
2Po+3P
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
Bond length in Bohr

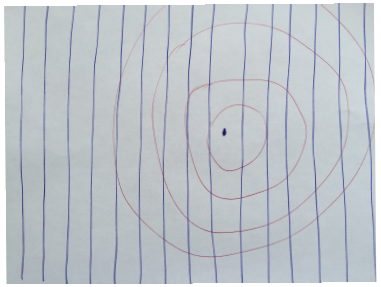

CO+ 2Pi
-112.2
-112.3
-112.4
-112.5
-112.6
-112.7
Total energy in Hartree
4P+3P
2Po+1S
3P+4So
2Po+1D
2Po+3P
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
Bond length in Bohr

Corrections to Born-Oppenheimer Approximation

- d/dr (and d^2/dr^2) ✔
- But wait, there's more!
- Angular Momentum
  - ℓ: orbital angular momentum of diatomic
  - $\vec{L}$: electronic orbital angular momentum
  - $\vec{S}$: electronic spin angular momentum
  - Hund's case a: J, S, Λ, Σ
  - J: vector sum of ℓ, $\vec{L}$, and $\vec{S}$
  - Λ: projection of $\vec{L}$ on internuclear axis
  - Σ: projection of $\vec{S}$ on internuclear axis
- Mass polarization: origin of electron coordinates
- Do these matter?

Solving nuclear Scattering Problem

- B.O. Approximation
  - $[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) - E + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}]F^\ell(r,E) = 0$
  - $\lim_{r\to 0} F^\ell(r,E) = 0$,
    $\lim_{r\to\infty} F^\ell(r,E) \propto h_\ell^{(-)}(kr) - \exp[2i\delta^\ell]h_\ell^{(+)}(kr)$, with
    $k^2 = \frac{2\mu E}{\hbar^2}$
  - $\frac{d\sigma}{d\Omega} = \left|f(E,\theta)\right|^2$
  - $f(E,\theta) = \frac{1}{2ik}\sum_{\ell=0}^{\infty}(2\ell+1)P_\ell(\cos\theta)\left(\exp[2i\delta^\ell] - 1\right)$
- 1^{st} order correction
  - $\ell(\ell+1) \to J(J+1)+S(S+1)-\Lambda^2-2\Lambda\Sigma-2\Sigma^2+\left\{\left\langle 0\middle|L_x^2+L_y^2\middle|0\right\rangle\right\}$
  - $\frac{d\sigma}{d\Omega} = ?$ 



Solving nuclear Scattering Problem

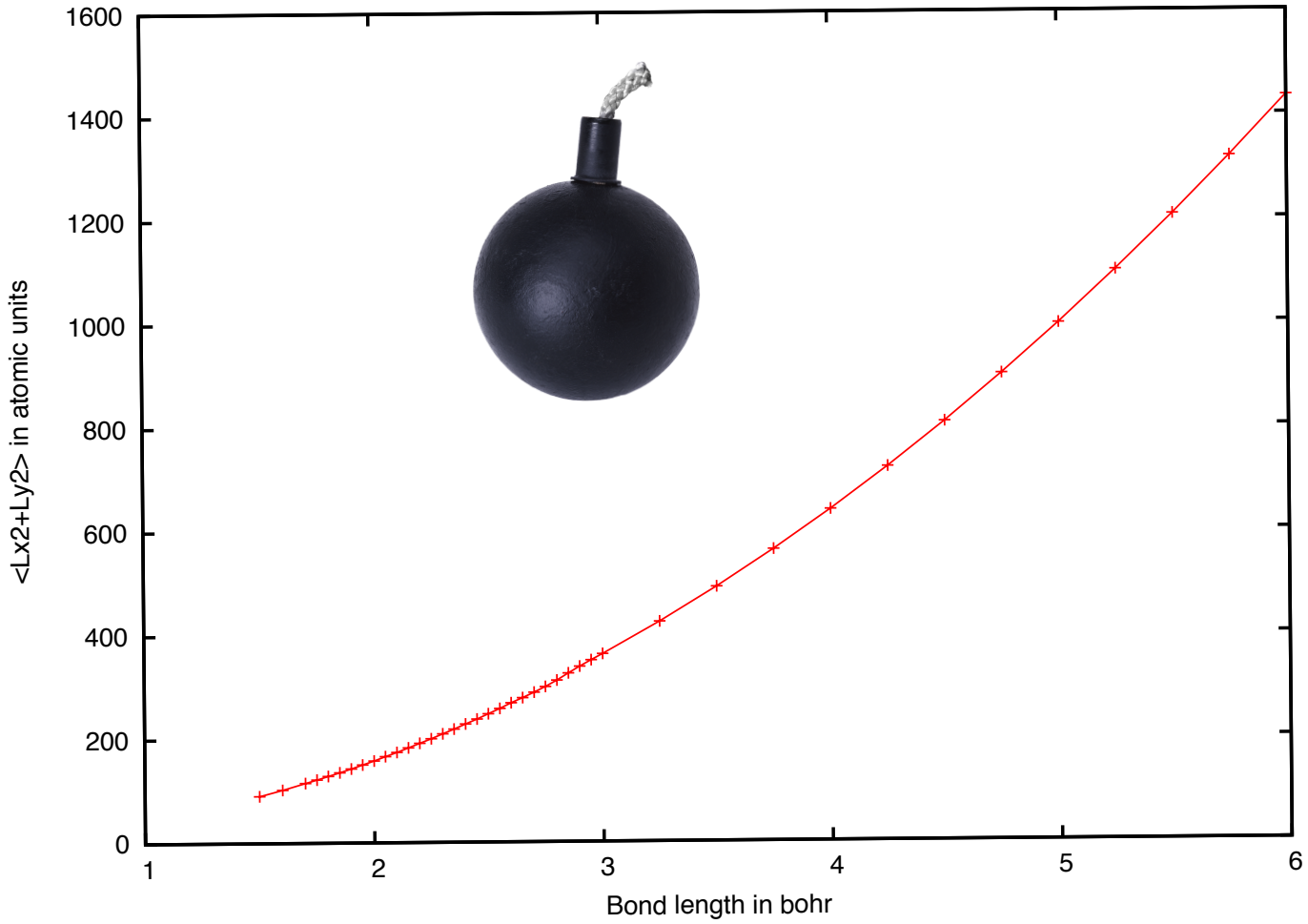
- B.O. Approximation
  - $[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) - E + \frac{\ell(\ell+1)\hbar^2}{2\mu r^2}]F^{\ell}(r,E) = 0$
  - $\lim_{r\to\infty} F^{\ell}(r,E) \propto h_{\ell}^{(-)}(kr) - \exp[2i\delta^{\ell}]h_{\ell}^{(+)}(kr)$, $k^2 = \frac{2\mu E}{\hbar^2}$
  - $\frac{d\sigma}{d\Omega} = \left|f(E,\theta)\right|^2$
  - $f(E,\theta) = \frac{1}{2ik}\sum_{\ell=0}^{\infty}(2\ell+1)P_{\ell}(\cos\theta)\left(\exp[2i\delta^{\ell}] - 1\right)$
- 1^{st} order correction
  - $\ell(\ell+1) \to J(J+1)+S(S+1)-\Lambda^2-2\Lambda\Sigma-2\Sigma^2+\left\{\left\langle 0\right|L_x^2+L_y^2\left|0\right\rangle\right\}$
  - $\frac{d\sigma}{d\Omega} =?$ 
- 2^{nd} order correction
  - $V \to V + \sum_n \frac{\left|\left\langle 0\right|T^r\left|n\right\rangle\right|^2}{V_n(r)-V_o(r)}$
  - but $\lim_{r\to\infty} \propto r^2$

- Well known problem without a solution

Solution to problem

- couple different Λ, Σ, (and S (so!));
- need matrix elements of $\left\langle n\middle|L_x^2+L_y^2\middle|m\right\rangle$ 

Computing $\left\langle n \middle| L_x^2 + L_y^2 \middle| n \right\rangle$



Defusing this bomb

- Mass polarization $\frac{1}{2} < n|\Sigma_{ij}\vec{v}_i \cdot \vec{v}_j|m > /M_{tot}$
  - atom-atom: $\frac{A}{M_A} + \frac{B}{M_B}$
  - diatomic: $\frac{A+B}{M_A+M_B}$
- $\frac{1}{3}$ comes from $\frac{1}{2\mu} < n|\frac{\partial^2}{\partial r^2}|m >$
- rest from $\frac{1}{2\mu r^2} < n|L_x^2 + L_y^2|n' >$
- $\lim_{r\to\infty} < n|L_x^2 + L_y^2|n' > = < n|L_{x,a}^2 + L_{y,a}^2|n' > + < n|MP_{xy}|n' > 2\mu r^2$
- when $< n|L_{x,a}^2 + L_{y,a}^2|n' > \propto \delta_{nn'}$, long range is pure

Conclusions

- We have a new powerful tool (MPEC) to treat complex systems
- We have the machinery to treat open-shell systems
- Dynamics calculations are underway