LS depolarizing transitions in A+H collisions: a diabatization approach

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Motivation

Discrepancy within calculations - Depolarization rates

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Why are they different?, Potential interaction

- *A*b initio calculations - Adiabatic representation
- Rayleigh-Schrödinger-Unsöld (RSU)

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Other sources

- Semiclassical theory
- Quantum dynamics theory

Literature

Semiclassical - Pertubation theory potential interaction

Perturbation theory potentials - Single electron model

- Brueckner, Anstee & O'Mara, Derouich et al., ...
- Good agreement at intermediate-long distances
- Some anomalies could arise because of the effect of avoided crossings and ionic effects

Literature

Semiclassical - Pertubation theory potential interaction

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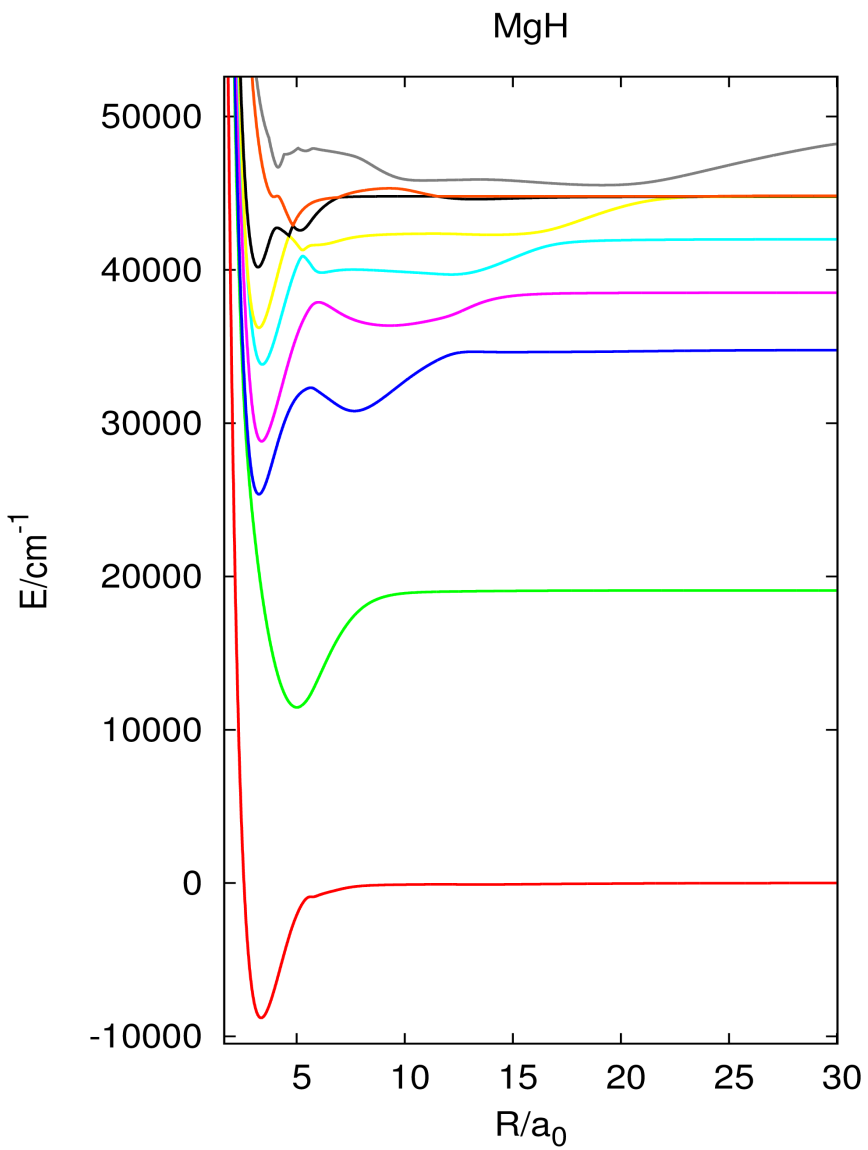
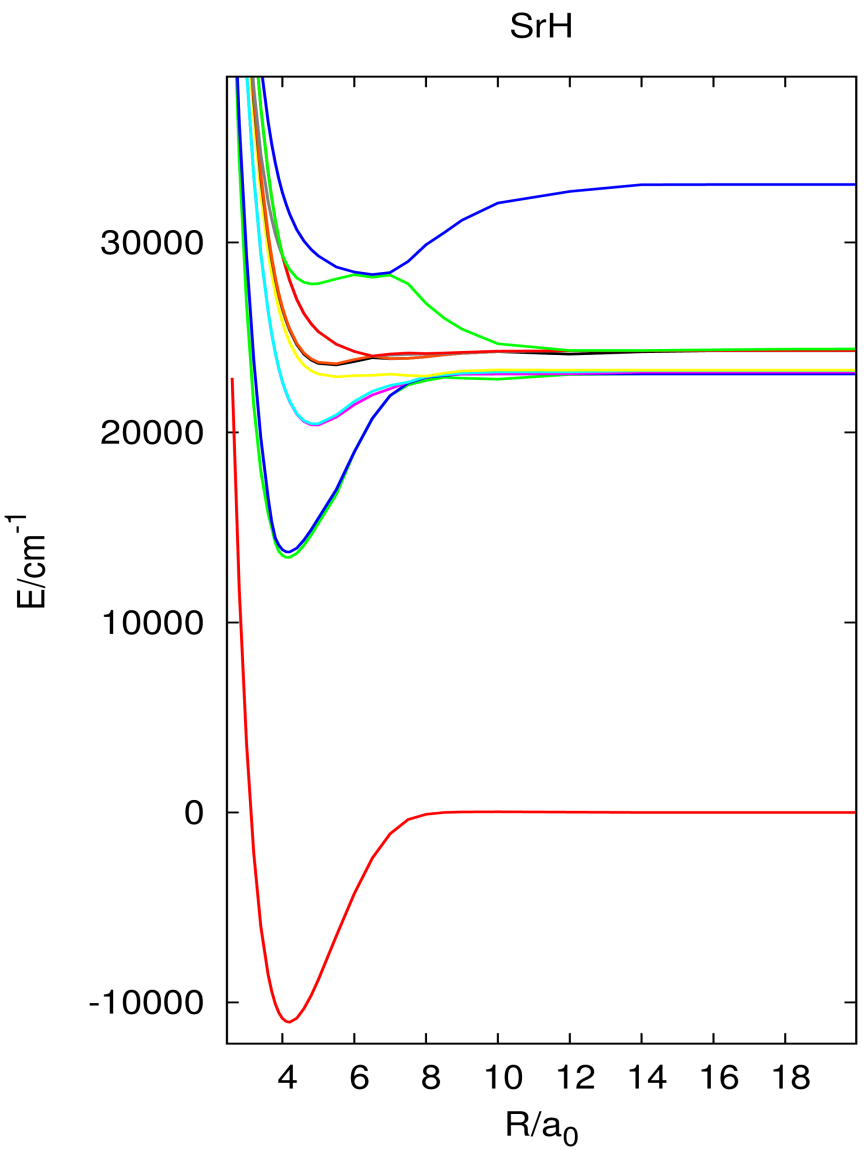
Quantum - Adiabatic potential interaction

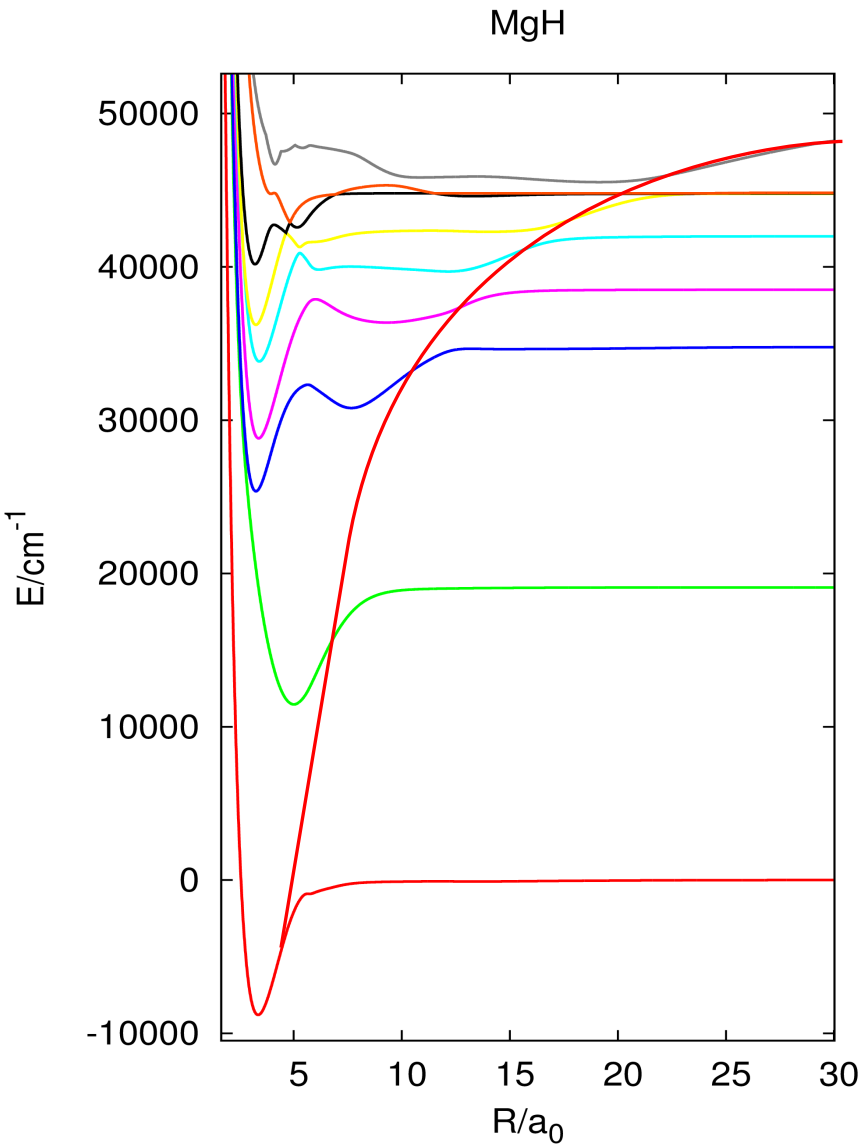
- Kerkeni and us
- Discrepancies due to curve crossing effects

Avoided crossings





Adiabatic curves



Abnormalities

- Avoided crossings
- $M^+ + H^-$ states cross with M(L, S) + H

Born-Oppenheimer approximation

TI Schrödinger equation - $H\Psi(r,R) = E\Psi(r,R)$

$$H = -\frac{\hbar^2}{2}\sum_i^{n_N}\frac{1}{m_i}\nabla^2_{R_i} - \frac{\hbar^2}{2m_e}\sum_i^{n_e}\nabla^2_{r_i} + V(r_1,...,r_{n_e},R_1,...,R_{n_N})$$

$$V = q_e^2\left[-\sum_i^{n_N}\sum_j^{n_e}\frac{\mathcal{Z}_i}{|R_i - r_j|} + \sum_{i,j>i}^{n_N}\frac{\mathcal{Z}_i\mathcal{Z}_j}{|R_i - R_j|} + \sum_{i,j>i}^{n_e}\frac{1}{|r_i - r_j|}\right]$$

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Nuclei are heavier so slower

$T_N = -\frac{\hbar^2}{2}\sum_i^{n_N}\frac{1}{m_i}\nabla_{R_i}^2$ neglected $\rightarrow \Psi_\alpha(r,R) \approx \varphi_{\alpha\alpha}(R)\phi_\alpha(r;R)$

$$H_e\phi_\alpha(r;R) = V(R)\phi_\alpha(r;R)$$

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V(R) is the potential energy curve/surface

Failing of Born-Oppenheimer approx.

Before considering Born-Oppenheimer approximation

$$\Psi_\beta(r,R) = \sum_\alpha \varphi_{\beta\alpha}(R)\phi_\alpha(r;R) \text{ with } \varphi_{\beta\alpha} \text{ satisfying}$$

$$\left[\langle\phi_\alpha(r;R)|\,T_N|\phi_{\alpha'}(r;R)\rangle + V(R) - E\right]\varphi_{\beta\alpha}(R) =$$

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BO considers: $\langle\phi_\alpha(r;R)|T_N|\phi_{\alpha'}(r;R) \approx \delta_{\alpha\alpha'}T_N$

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To evaluate kinetic couplings we use commutator $[T_N, H_e]$

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couplings are large when electronic states are close

Ab initio calculations

Main steps for the calculation of potential interaction

- Electronic structure package - Molpro, Molcas, Gaussian

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In our studies

- (Mg, Sr, H - Dunning basis, Ca - Ahlrichs "def2" basis,
  Ba - Pseudopotential (10 e^-) + basis
- Configuration Interaction (CI) calculations

Diabatization with MOLPRO

Method

Quasi-diabatization method based on the maximization of the overlap between states at a certain geometry with respect to the overlap at a reference geometry

Cons

- The method cannot be manipulate
- Presence of ionic crossing state troubles the method
- Diabatic states are not smooth
- Expensive method - 2 steps:
  - Maximization of overlap
  - DDR to find transformation - Double number of points

Pros

- Method is automatic

Diabatization with our method

Method

NACME are obtained as the solution of a second order diferential equation which only requires the overlap matrix and its derivatives

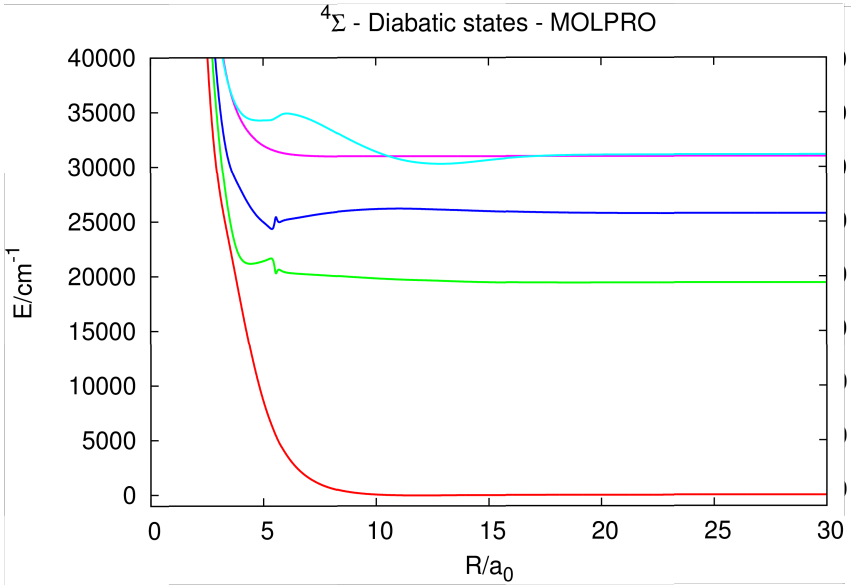
Cons

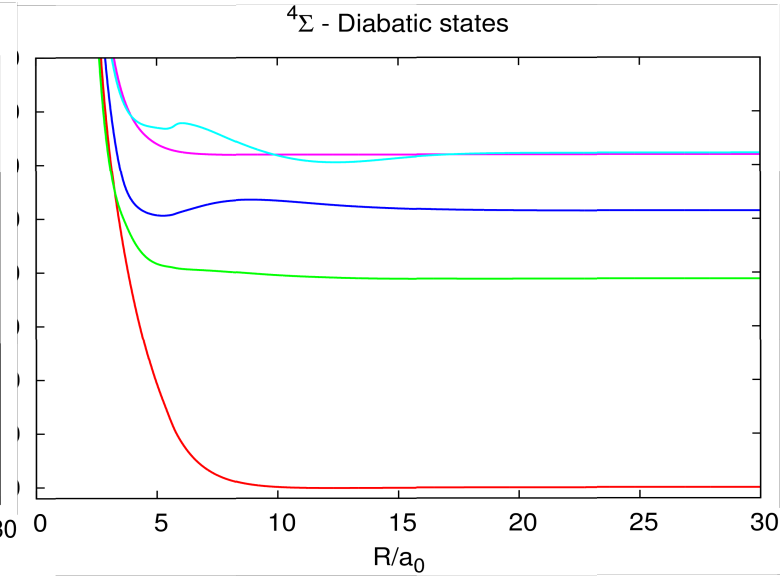
- Overlap matrix requires manipulation
- Presence of ionic crossing state troubles the method
- It requires the computation of many points

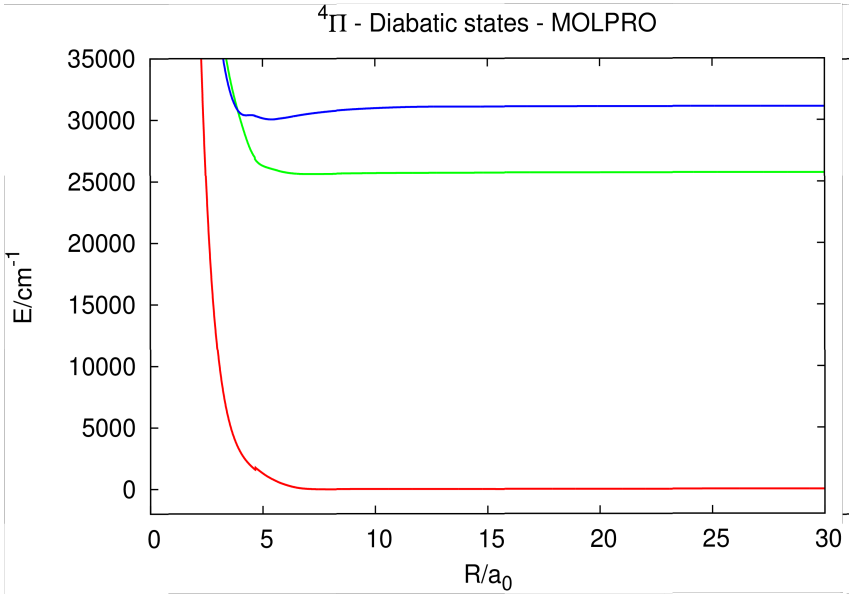
Pros

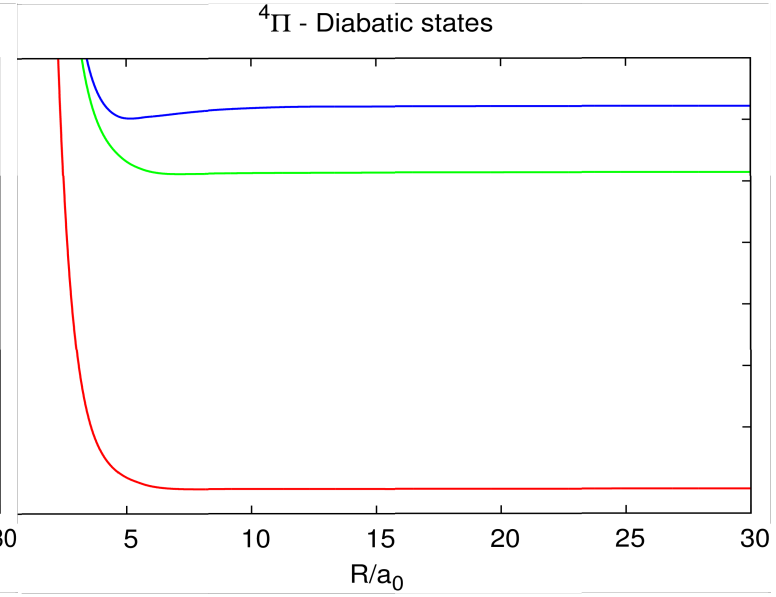
- Diabatic states are smooth

Diabatic states

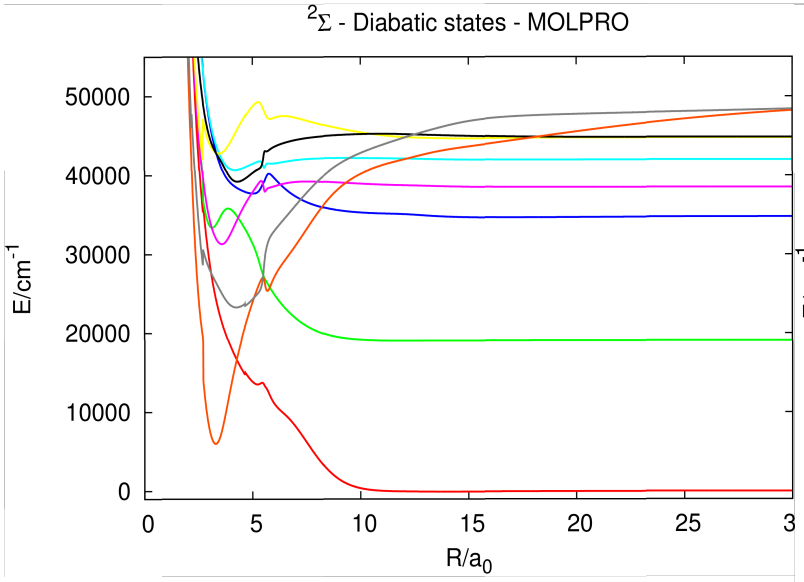


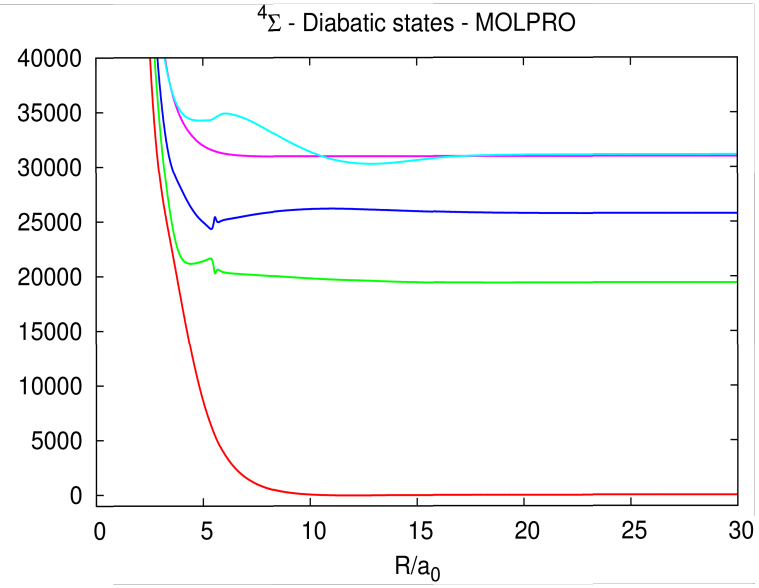


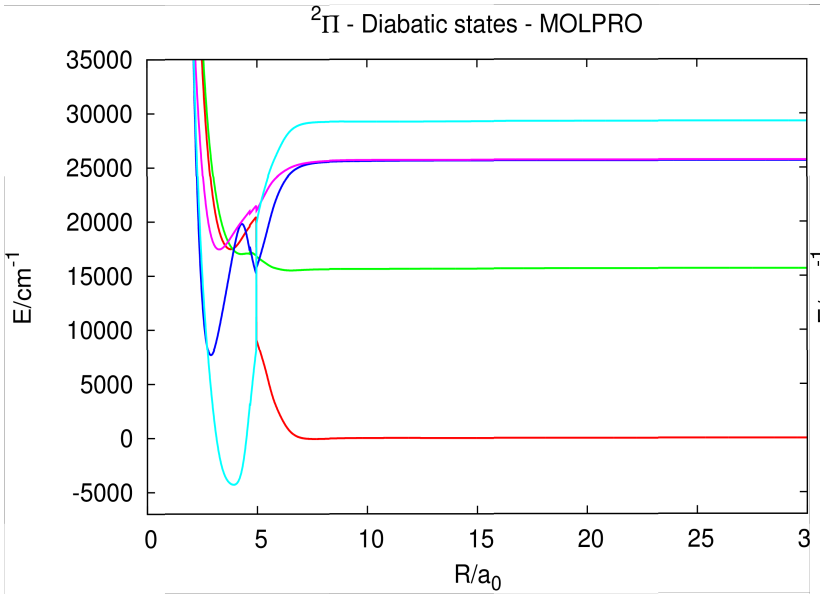


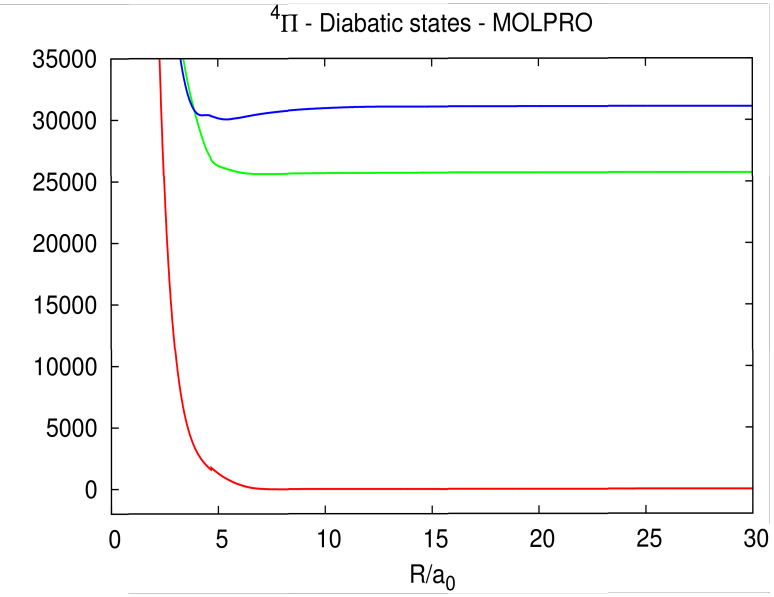


Diabatic states - MOLPRO









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