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# Theoretical studies on electron collisions with molecular ions

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November 20 -2009

## *How do we perform these calculations?*

- Solve the electronic problem. Determine potential energy surfaces, autoionization widths and couplings
- Study the nuclear dynamics using wave packet propagation.

Example:      $\text{BeH}^+$

Triatomic system  $\text{XH}_2^+$

## Dissociative recombination of BeH<sup>+</sup>



- Be is a primary choice for the first wall at the ITER fusion reactor
- Be will enter the plasma and react with hydrogen
  - ➔ BeH<sup>+</sup> will be formed in the edge plasma.
- How effectively is BeH<sup>+</sup> destroyed by DR?
- Toxicity of Be
  - ➔ No experimental studies exist
  - ➔ Need for theory.

# Dissociative recombination of BeH<sup>+</sup>



PHYSICAL REVIEW A 80, 012501 (2009)

## Dissociative recombination of BeH<sup>+</sup>

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# Computational flowchart

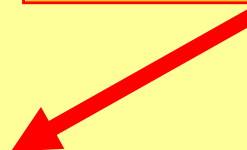
Structure calculations  
Electronically bound states

Electron scattering calc.  
Resonant states

Diabatization  
Potentials, couplings, widths

Dynamics calculation (wave  
packet propagation)

Cross section for the reaction, final state distribution



# Structure calculations

MRCI calculation using  
natural orbitals of the ionic  
groundstate.

Reference space:


$1\sigma, 2\sigma, 3\sigma, 1\pi, 4\sigma, 5\sigma$

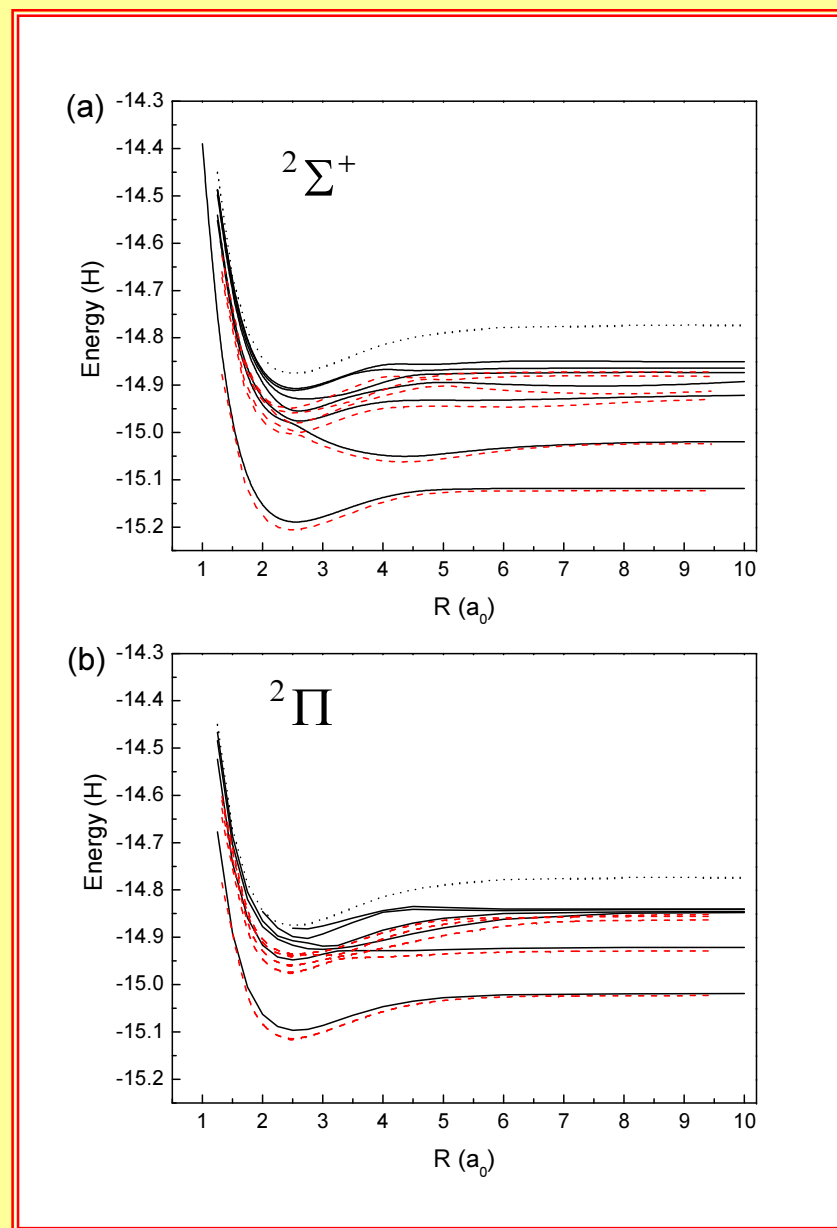
+ single excitations

Basis set:

H:  $(6s, 3p, 1d) \rightarrow [5s, 3p, 1d]$

Be:  $(14s, 7p, 2d) \rightarrow [7s, 4p, 2d]$

 Electronically bound states



# Electron scattering calculations

Using the Complex Kohn variational method, the resonant states of BeH are calculated.

Trial wave function:

$$\Psi_{\Gamma_0} = \sum_{\Gamma} A \left\{ \Phi_{\Gamma}(\mathbf{r}_1 \dots \mathbf{r}_N) F_{\Gamma\Gamma_0}(\mathbf{r}_{N+1}) \right\} + \sum_{\mu} d_{\mu}^{\Gamma_0} \Theta_{\mu}(\mathbf{r}_1 \dots \mathbf{r}_{N+1})$$

Target wave function  
MRCI

Correlation and polarization

$$F_{\Gamma\Gamma_0}(\mathbf{r}) = \sum_i c_i^{\Gamma\Gamma_0} \varphi_i(\mathbf{r}) + [f_l^-(k_{\Gamma}r) \delta_{ll_0} \delta_{mm_0} + T_{ll_0mm_0}^{\Gamma\Gamma_0} f_l^+(k_{\Gamma}r)] Y_{l,m}(\hat{\mathbf{r}}) / r$$

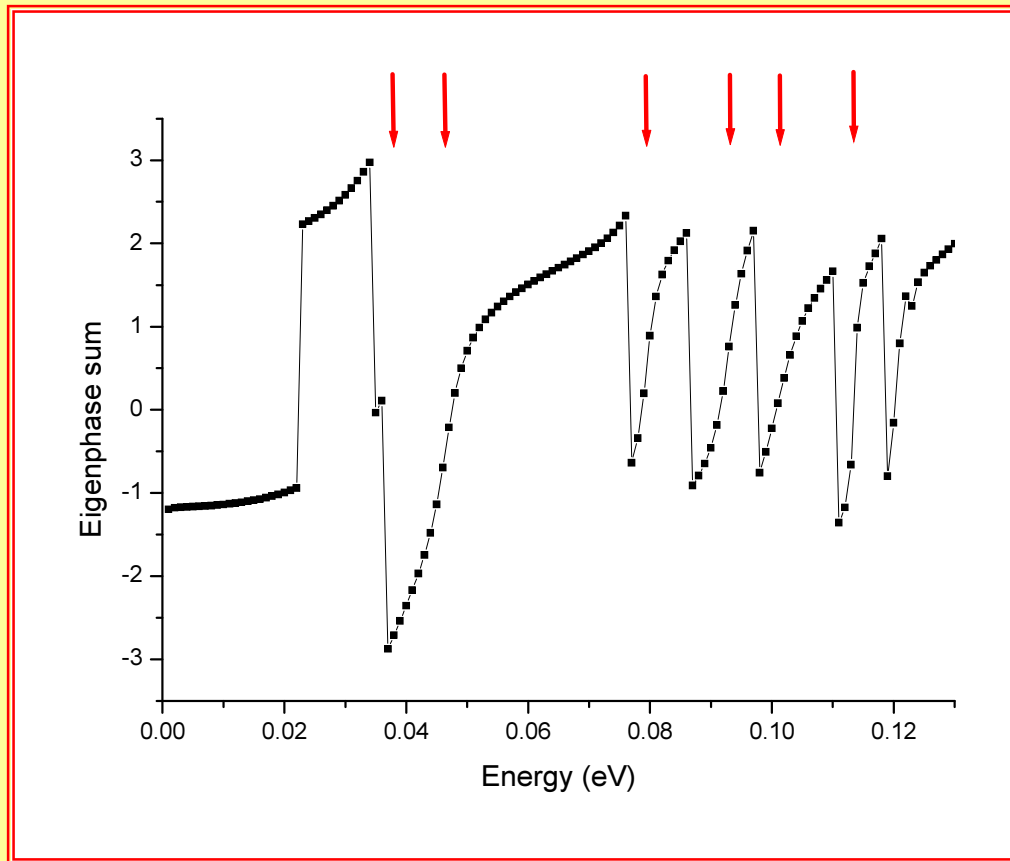
Insert into a variational functional for the T-matrix  $\Rightarrow c_i, d_{\mu}, T$

Eigenphase sum of the T-matrix:  $\Rightarrow E_{\text{res}}(\mathbf{R}), \Gamma_{\text{res}}(\mathbf{R})$

# Electron scattering calculations

Eigenphase sum:  ${}^2A_1$  symmetry ( ${}^2\Sigma^+$ ,  ${}^2\Delta$ )  $R = 2.5 a_0$

Breit-Wigner: 
$$\delta(E) = \delta_{res}(E) + \delta_{bg}(E) = \tan^{-1}\left(\frac{\Gamma}{2(E - E_{res})}\right) + a + bE + cE^2$$

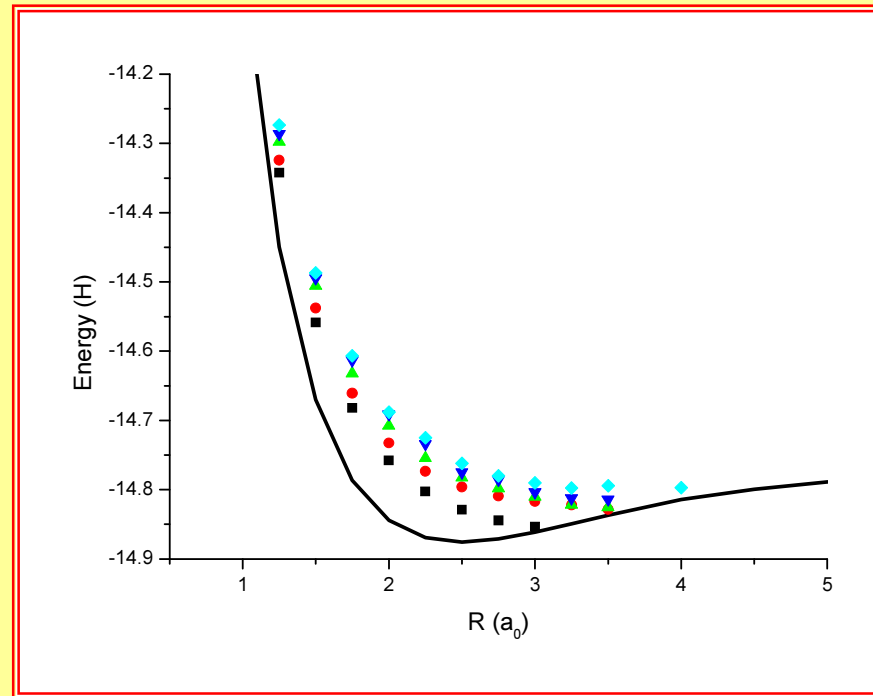


$E_{res}(R), \Gamma(R)$

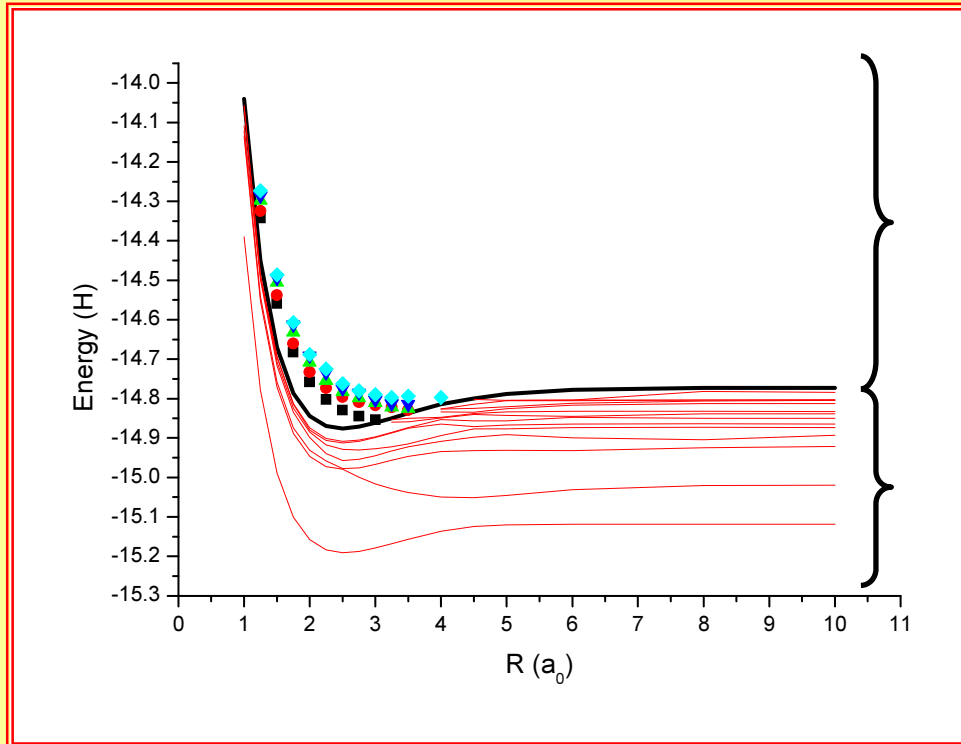


# Electron scattering calculations

Resonant states of  $2\Sigma^+$  symmetry.



# Diabatization



Resonant states from  
electron scattering calculations

Adiabatic electronically  
bound states from structure  
calculations

In order to describe DR, we transform these potentials to *diabatic potentials*.

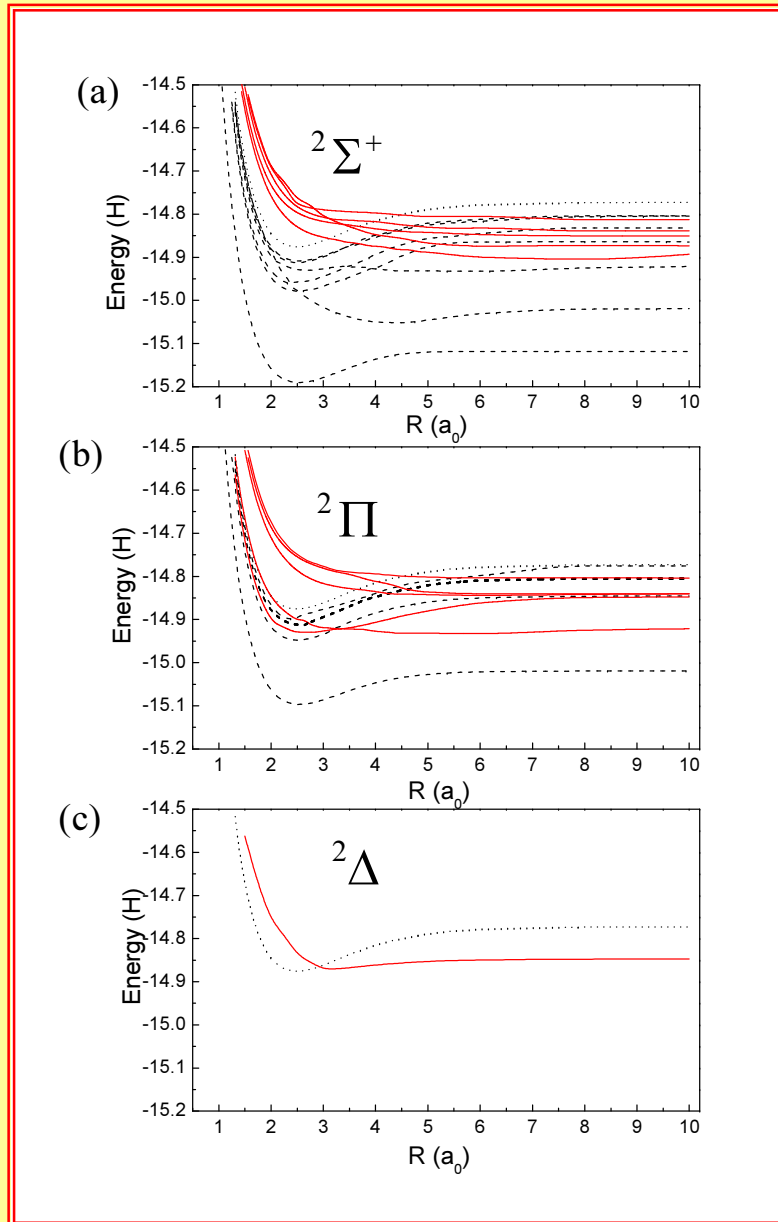
Configuration of the groundstate ion:  $(1\sigma)^2(2\sigma)^2$

# Diabatization

Diabatic potential energy curves.

  $V_i(R)$

The diabatic states will couple by electronic couplings  $V_{ij}(R)$



# Diabatization

- Estimate the quasidiabatic potentials by following the configurations of the resonant states.

$$\text{red arrow} \rightarrow V_i(R)$$

- Unitary transformation:

$$\Phi^{qd} = \mathbf{T}\Phi^{ad} \quad \text{red arrow} \quad \mathbf{V} = \mathbf{T}^{-1}\mathbf{U}\mathbf{T}$$

- Assume the transformation matrix can be written as product of matrices describing successive 2x2 rotations.

$$\mathbf{T} = \mathbf{T}_1\mathbf{T}_2\mathbf{T}_3 \cdots \quad \mathbf{T}_i = \begin{pmatrix} \cos \gamma_i & -\sin \gamma_i & 0 & \cdots \\ \sin \gamma_i & \cos \gamma_i & 0 & \cdots \\ 0 & 0 & 1 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}$$

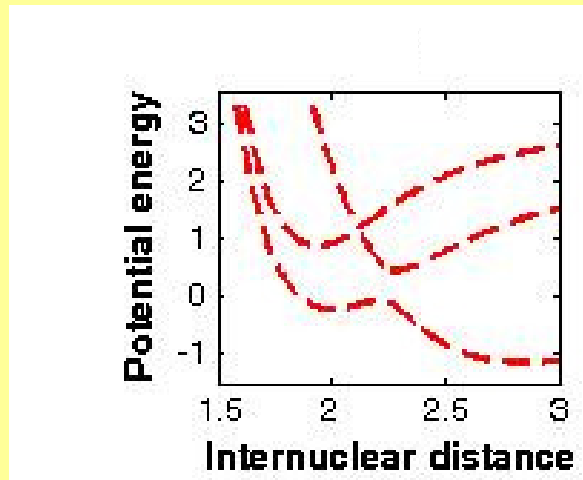
Assume  $\gamma_i(R) = \frac{\pi}{4} [1 + \tanh(\alpha_i(R - R_i))]$

# Diabatization

Adiabatic potentials  $U$

$$V_1 = \mathbf{T}_1^{-1} \mathbf{U} \mathbf{T}_1$$

$$V_2 = \mathbf{T}_2^{-1} \mathbf{T}_1^{-1} \mathbf{U} \mathbf{T}_1 \mathbf{T}_2$$




# Diabatization

- Set up the transformation matrix  $\mathbf{T} = \mathbf{T}_1 \mathbf{T}_2 \cdots = \mathbf{T}(\alpha_1, R_1, \alpha_2, R_2, \dots)$

  $\mathbf{V} = \mathbf{T}^{-1} \mathbf{U} \mathbf{T}$

- Optimize the agreement with the estimated quasidiabatic potentials

 Electronic couplings  $V_{ij}(R)$

*We now have:*      *potential curves*       $V_i(R)$

*electronic couplings*       $V_{ij}(R)$

*autoionization widths*       $\Gamma_i(R)$

# Molecular dynamics

To describe the molecular dynamics, wave packets are propagated on the coupled potentials.

Electron capture: Initial condition

$$\Psi_i(t=0, R) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{v=0}(R) \leftarrow \text{Vibrational wavefunction of the ion}$$

Wave packet propagation:

$$i \frac{\partial}{\partial t} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \end{pmatrix} = \begin{pmatrix} \hat{T} + W_1 & c_{12} & \cdots \\ c_{21} & \hat{T} + W_2 & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \end{pmatrix}$$

Autoionization.  $W_i(R) = E_i(R) - i \frac{\Gamma_i(R)}{2}$

# Molecular dynamics

The cross section is calculated by *i.e.* projecting the asymptotic wave packet onto the energy-normalized wave function of the ion-pair potential.

$$\sigma_i(E) = \frac{2\pi^3}{E} g \left| \langle \Phi_i^E | \Psi_i(t_\infty) \rangle \right|^2$$

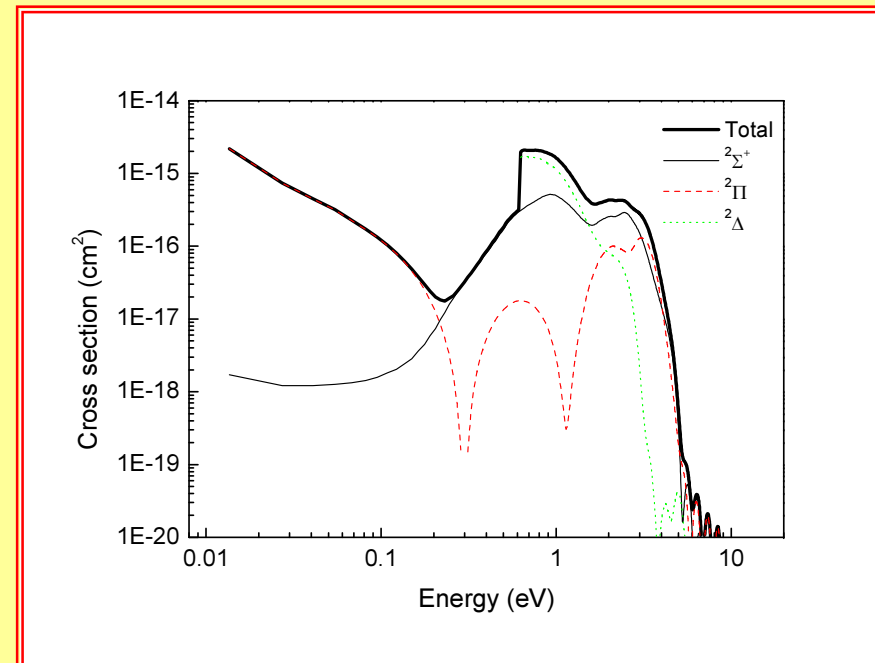
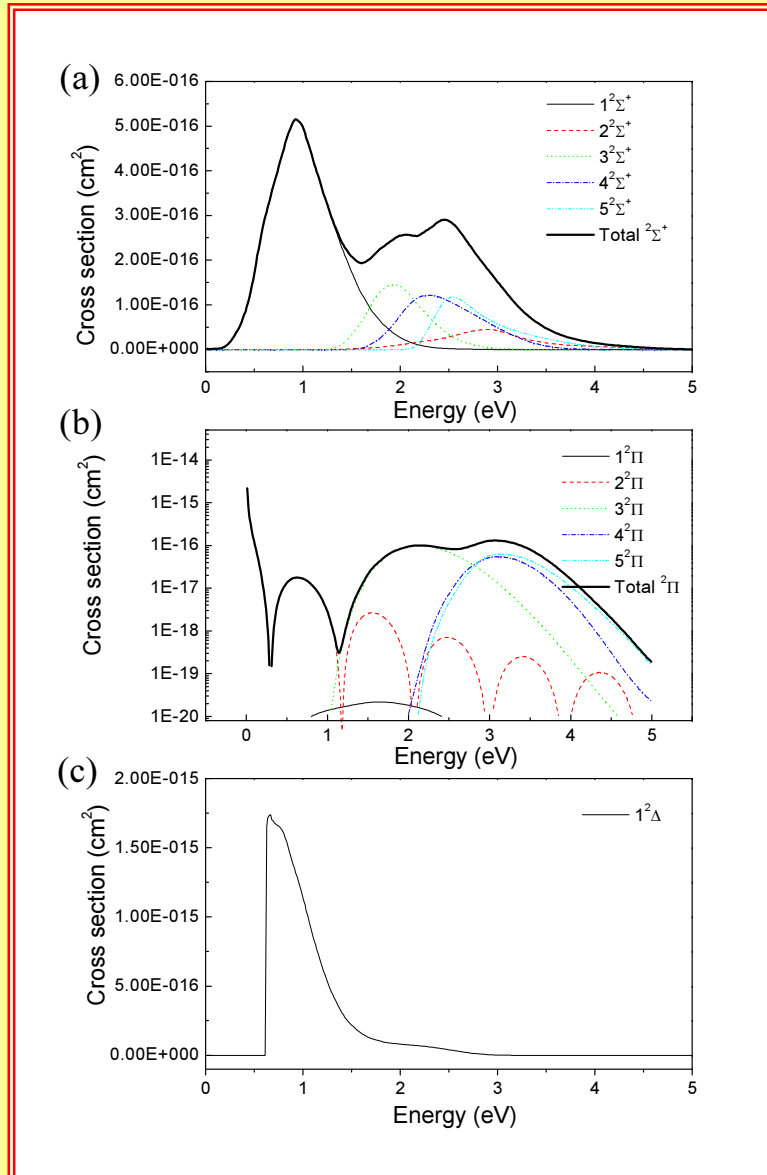


# Results

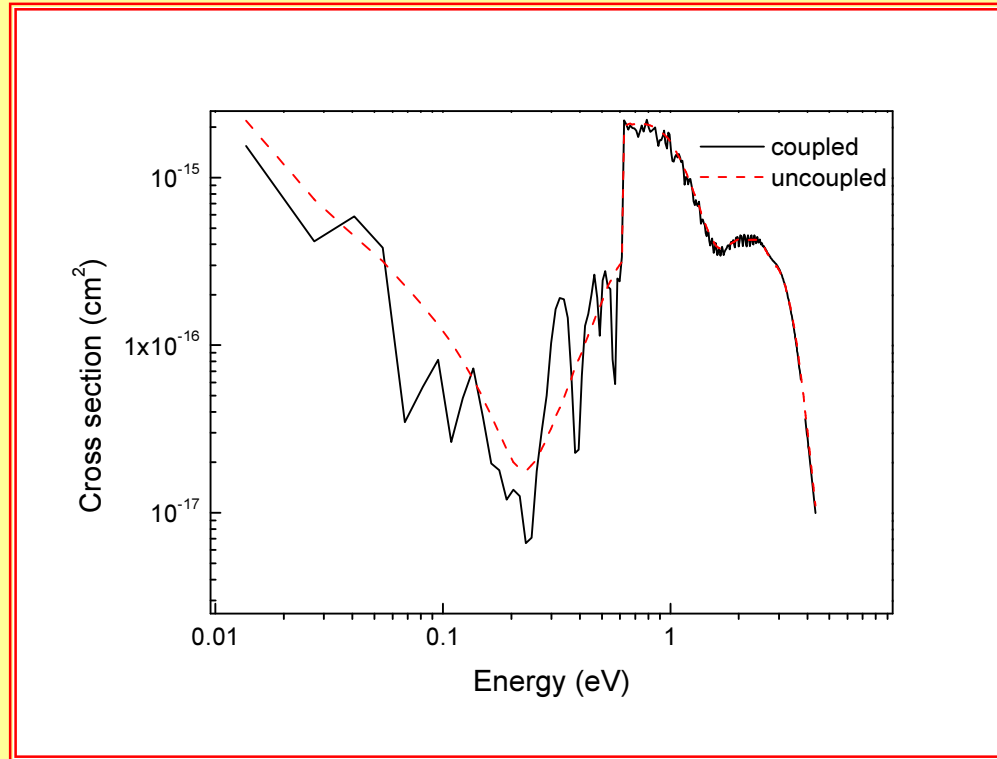
Uncoupled potentials

Cross section from each state

Total cross section



# Results



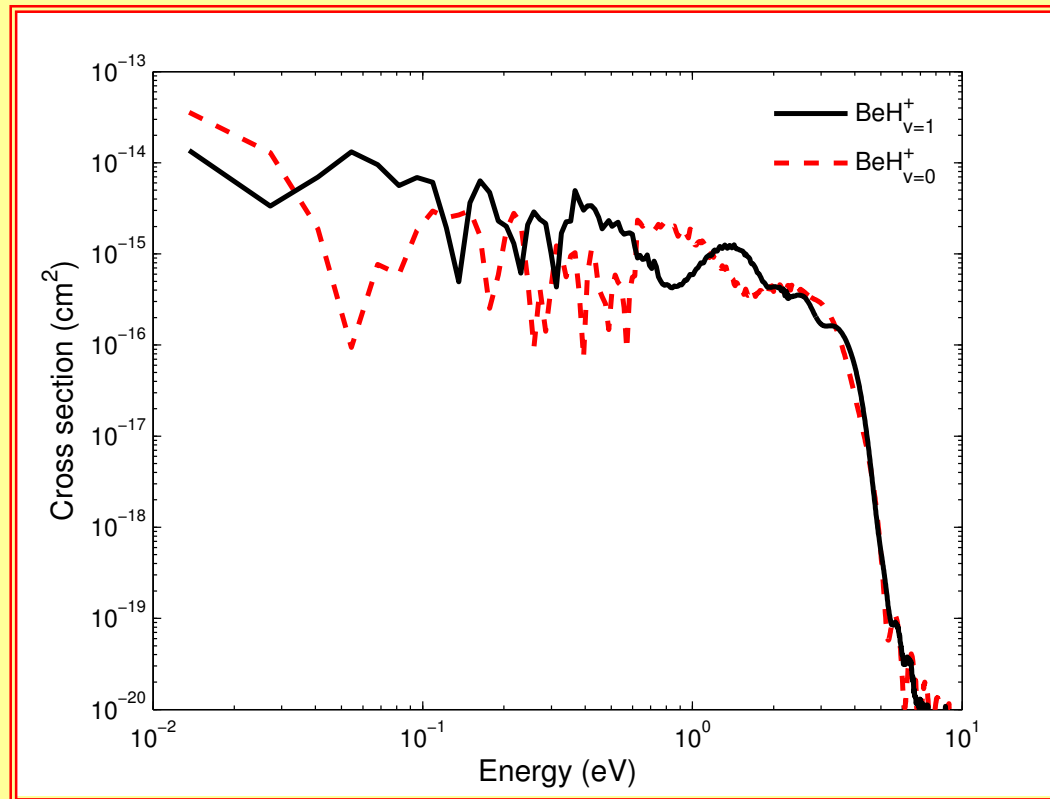
Effect of the electronic couplings

➡ Oscillations

➡ No change in magnitude.

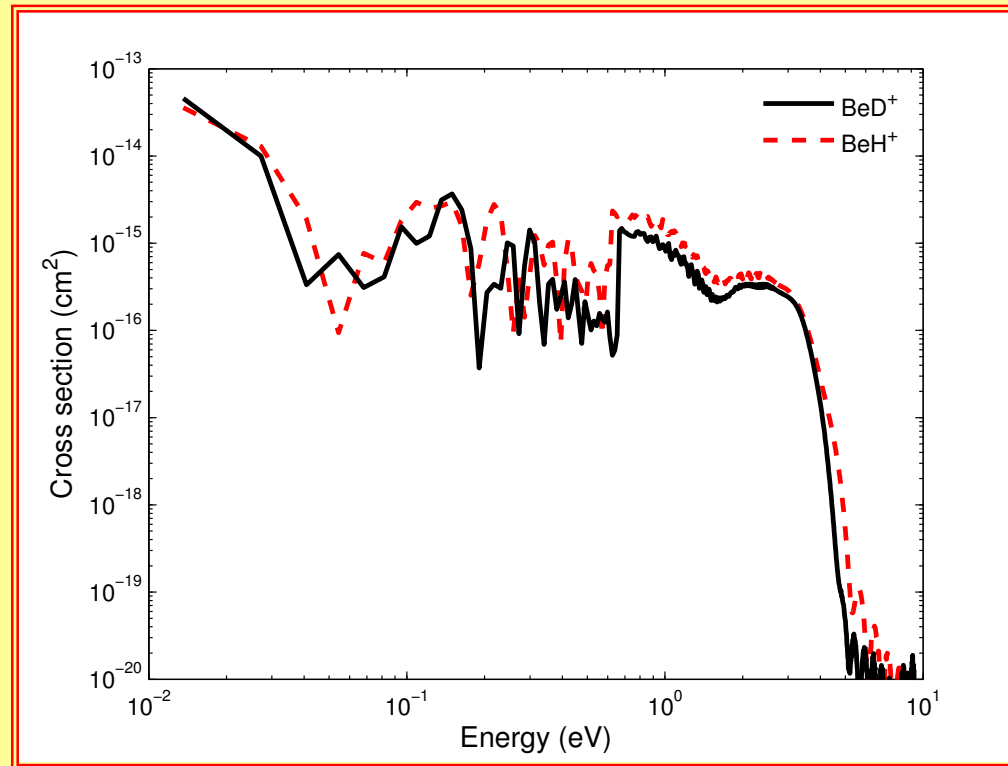
# Results

Vibrationally excited ions  $\Psi_i(t=0, R) = \sqrt{\frac{\Gamma_i(R)}{2\pi}} \chi_{v=1}(R)$



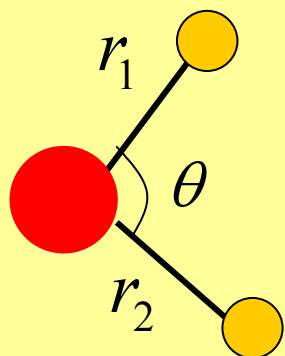
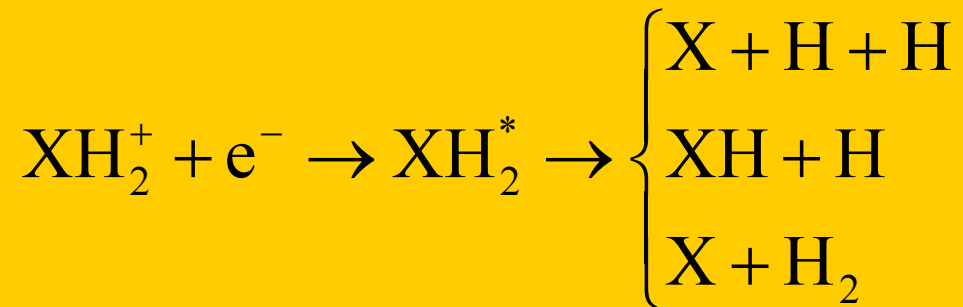
# Results

DR of  $\text{BeD}^+$   $\mu_{\text{BeD}}$



# Dissociative recombination of $\text{XH}_2^+$

Where  $X = \text{Be}$  or  $\text{C}$




# Dissociative recombination of $\text{BeH}_2^+$

To study DR of a polyatomic system is demanding

- also for a triatomic molecule

3 dimensions:  $r_1, r_2, \theta$

- The quantum chemistry and electron scattering calculations have to be performed in all three dimensions

  $N^3$  calculations

- Diabatization that is “consistent” for all dimensions

# Dissociative recombination of $\text{BeH}_2^+$

Multi-dimensional wave packet propagation on coupled potentials.

MCTDH (Multi-Configuration Time-Dependent Hartree)

$$\Psi(t, r_1, r_2, \theta) = \sum_{i=1}^{n_{r1}} \sum_{j=1}^{n_{r2}} \sum_{k=1}^{n_{\theta}} A_{ijk}(t) \varphi_i^{(r1)}(t, r_1) \varphi_j^{(r2)}(t, r_2) \varphi_k^{(\theta)}(t, \theta)$$

Coefficients

Single-particle functions. Are represented in a DVR basis

The Hamiltonian has to be given in a “product form”

$$H(r_1, r_2, \theta) = \sum_{i=1}^{n_{r1}} \sum_{j=1}^{n_{r2}} \sum_{k=1}^{n_{\theta}} h_{ijk} f_i(r_1) g_j(r_2) h_k(\theta)$$

## Summary

I have described how we run the calculations by performing structure calculations and electron scattering calculations. We then combine these by performing a diabaticization technique.

The dynamics is carried out by wave packet propagation.

The results from calculations on DR of  $\text{BeH}^+$  were shown.

The calculations are much more complex when we study DR of  $\text{XH}_2^+$ , where  $\text{X} = \text{C}$  or  $\text{Be}$ .

### **In collaboration with ...**

Dr. Johanna Brinne Roos (Stockholm University)

Prof. Ann E. Orel (University of California, Davis)

Prof. Mats Larsson (Stockholm University)