

IAEA Technical Meeting on Uncertainty Assessment  
and Benchmark Experiments for Atomic and  
Molecular Data for Fusion Applications

**Uncertainty evaluation in  
theoretical calculations of cross  
sections for  
electron-molecule collisions**

**V. Kokoouline**

***Department of Physics, University of Central Florida, Orlando, FL***

# Processes of interest

- \*Elastic and momentum transfer collisions
- \*Inelastic rotational excitation
- \*Inelastic vibrational excitation
- \*Dissociative electron attachment or recombination
- \*Radiative electron recombination, photoionization
- \*Inelastic, electronic excitation
- \*Impact dissociation, which normally goes via electronic excitation
- \*Ionization

# Many difficulties for UQ in e-molecule collisions

- \*Uncertainty in target properties (energy levels, polarizability, dipole and higher moments)
- \*Consistency in the treatment of the N-electron target versus the (N+1)-electron collision problem
- \*The role of the nuclear motion in electron-molecule collisions
- \*Numerical uncertainties

# Suggestions

- \*Calculations to be performed for different target models.
- \*Quantify uncertainties associated with the choice of the scattering model.
- \*Use a family of basis sets, such as (aug)-cc-pVxZ (x=2,3,...).
- \*At low electron energies, vibrational motion should be accounted for.

# Nuclear motion

- \*Electronic resonances can greatly enhance vibrational excitation cross sections and these can be computed in a relatively straightforward fashion using resonance curves.
- \*Conversely, nonresonant vibrational excitation can be treated by vibrationally averaging S-matrices as a function of geometry (frame transformation).
- \*In a similar way, rotational excitation can be treated by a frame transformation.
- \*An efficient method that unifies nonresonant and resonant processes in electron-molecule scattering is the quantum defect approach (QDT).
- \*Uncertainties are mainly determined by uncertainties of the geometry-fixed S-matrices.  $\Delta\sigma/\sigma \sim 2|\Delta S|/|S|$ .

# Evaluation of uncertainties within a chosen model

If there are not that many parameters, one can simply vary them within a reasonable interval and see the effect of the variation on the final results (cross sections). It is a sort of sensitivity test.

## Systematic approaches:

- \* Least squares method
- \* Monte-Carlo methods

# Example 1: Vibrational excitation of HeH<sup>+</sup> by an electron impact

If rotational structure is neglected (averaging over initial rotational states and summed over final states), the cross is

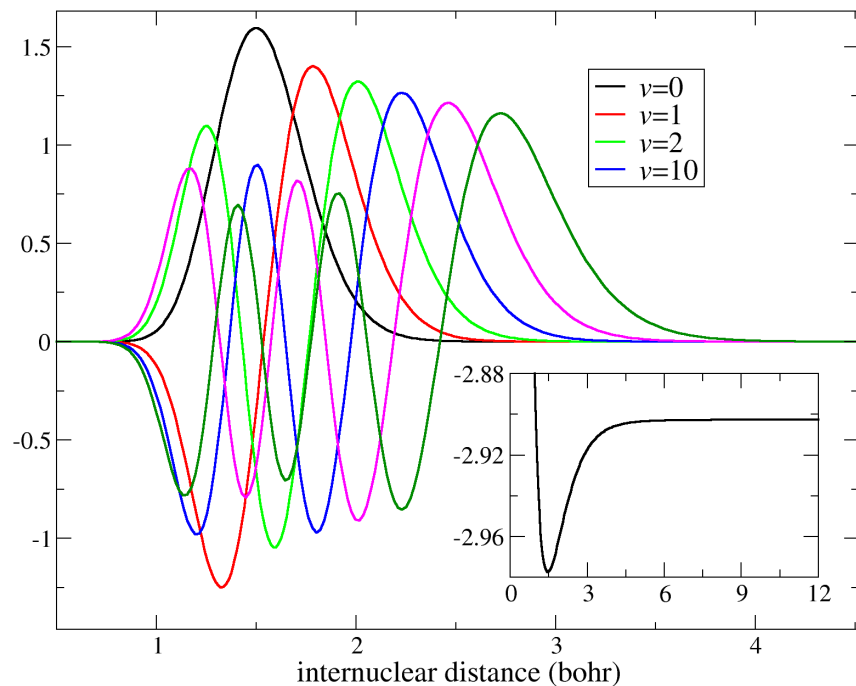
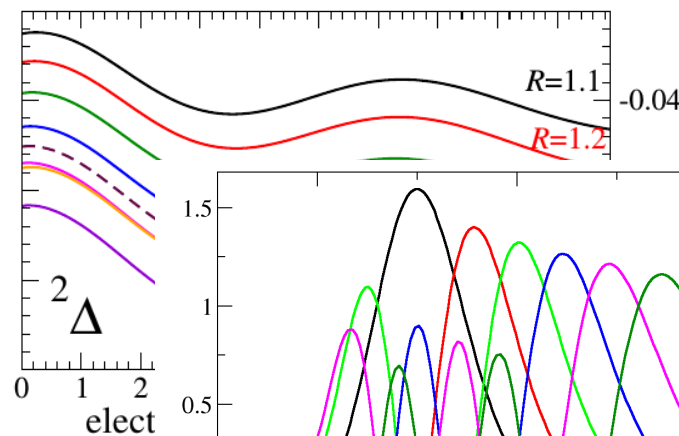
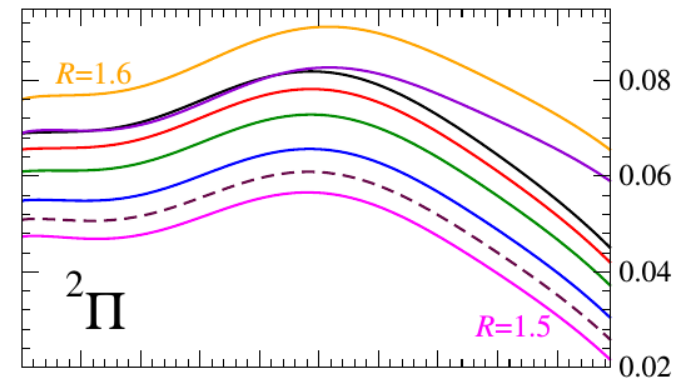
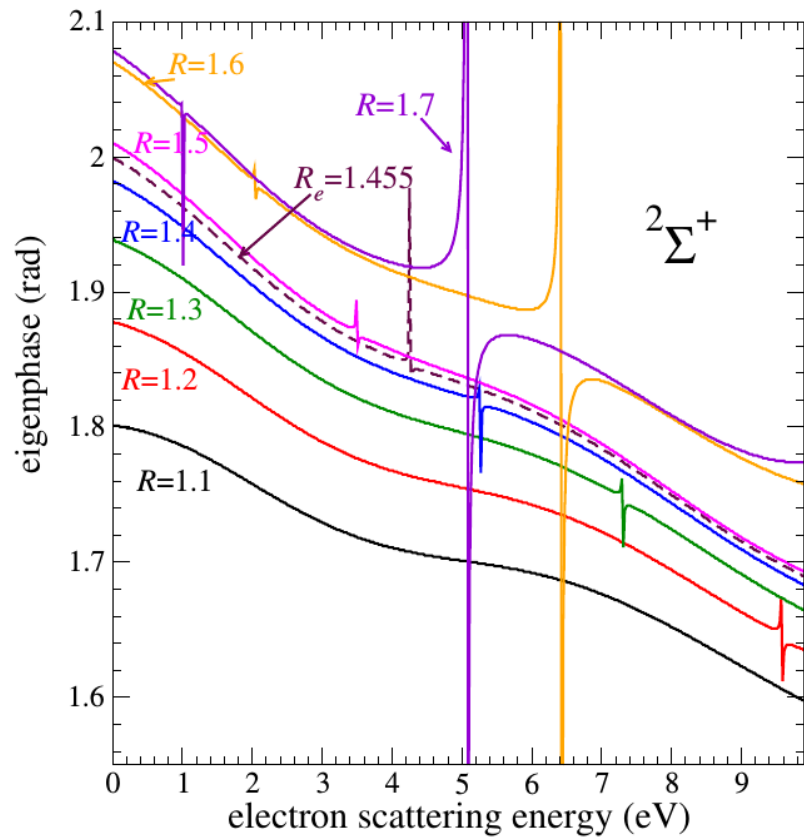
$$\sigma_{v'v}(E_{el}) = \frac{\pi\hbar^2}{2m_e E_{el}} \sum_{\Lambda'l'\Lambda l} \left| \mathcal{S}_{\Lambda'l'v',\Lambda l v}^{phys} - \delta_{\Lambda l v, \Lambda'l'v'} \right|^2$$

$$\mathcal{S}_{\Lambda'l'v',\Lambda l v} = \langle \psi_{v'}(R) | \mathcal{S}_{\Lambda'l',\Lambda l}(R) | \psi_v(R) \rangle$$

$$\mathbf{S}(R) = (\mathbf{1} + i\mathbf{K}(R))(\mathbf{1} - i\mathbf{K}(R))^{-1}$$

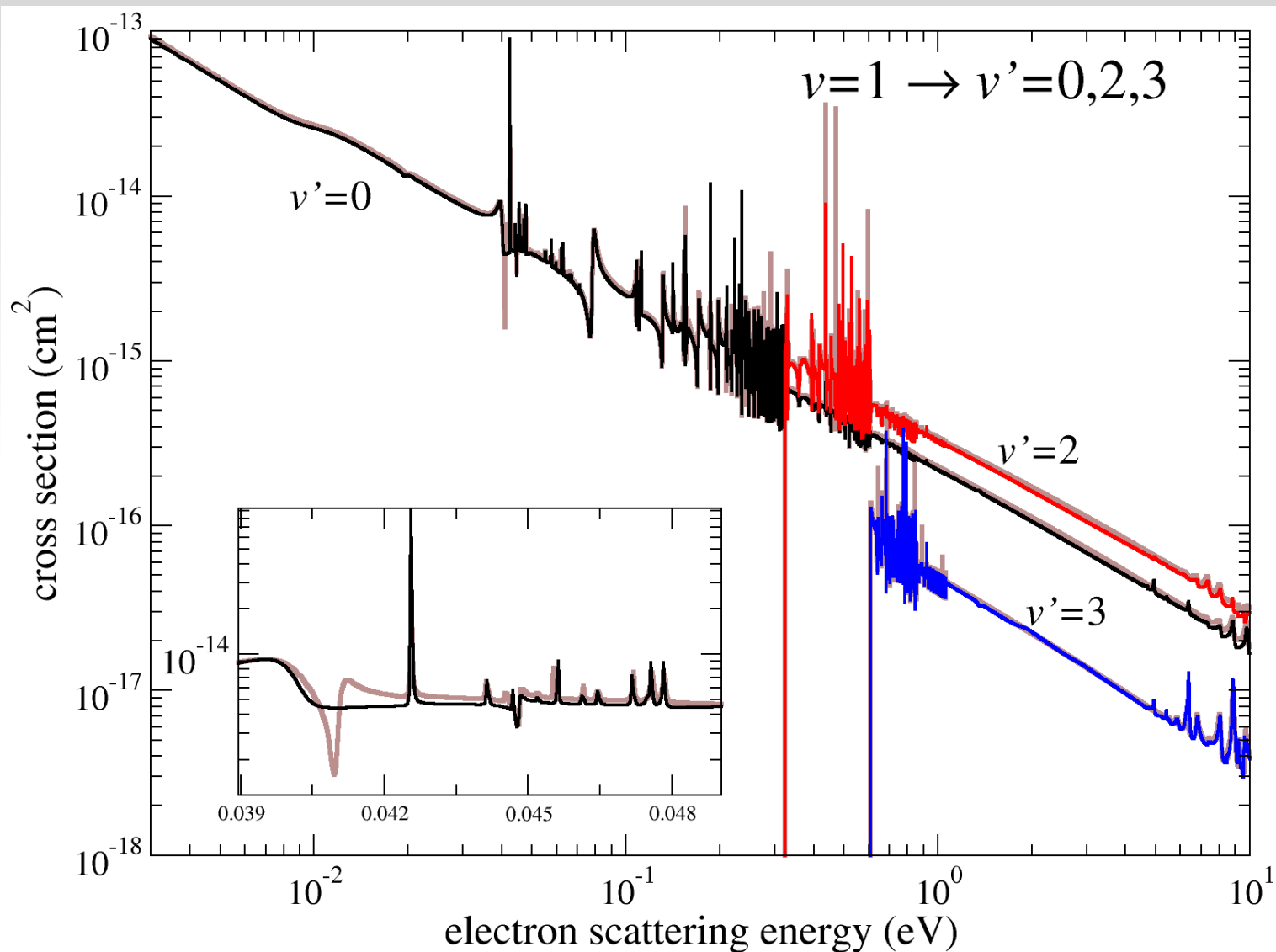
$$\mathcal{S}^{phys}(E) = \mathcal{S}^{oo} - \mathcal{S}^{oc} \left[ \mathcal{S}^{cc} - e^{-2i\beta(E)} \right]^{-1} \mathcal{S}^{co} \quad \mathcal{S} = \begin{pmatrix} \mathcal{S}^{oo} & \mathcal{S}^{oc} \\ \mathcal{S}^{co} & \mathcal{S}^{cc} \end{pmatrix}$$

# Dependence on the internuclear distance





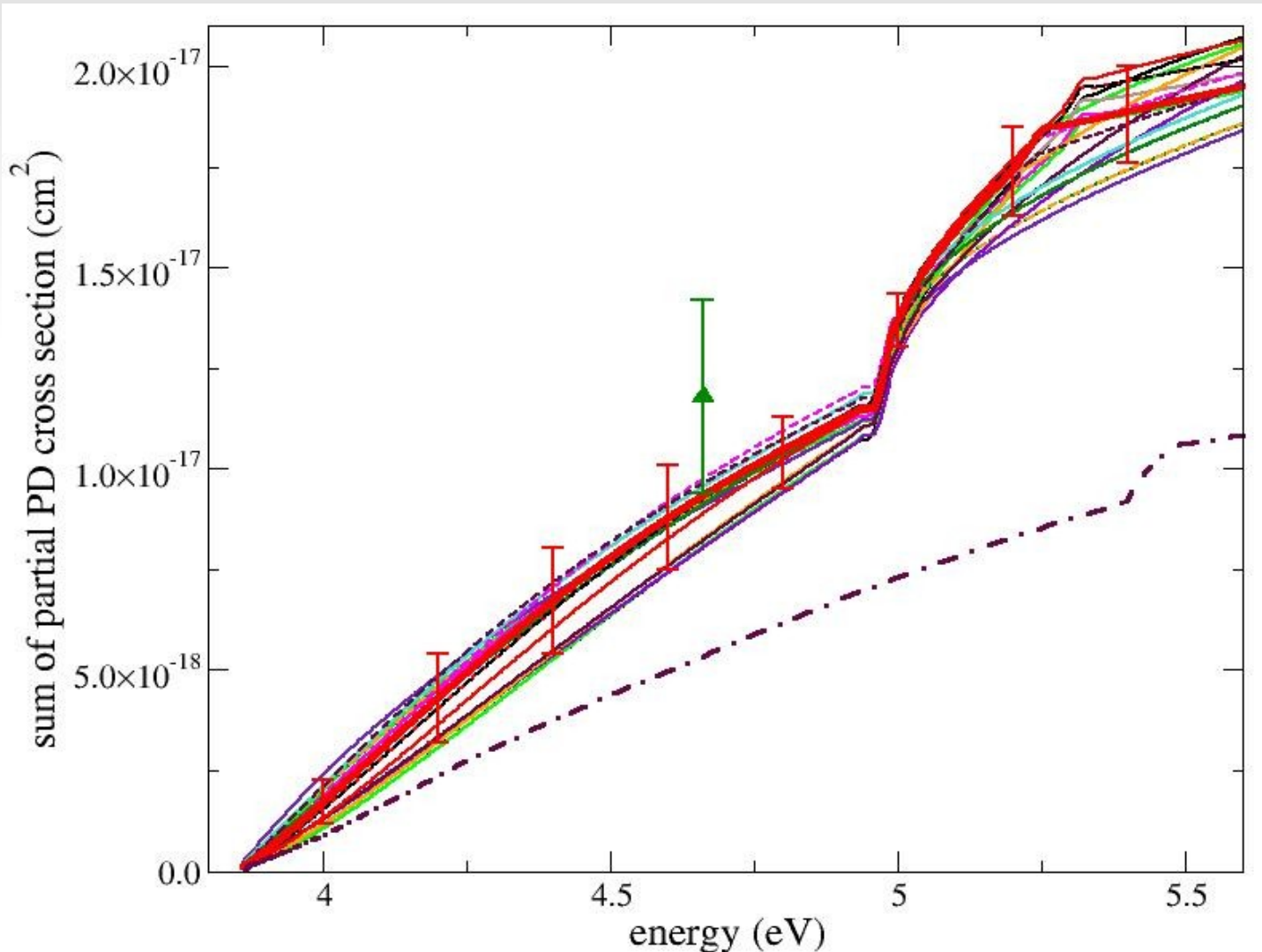
# Cross section



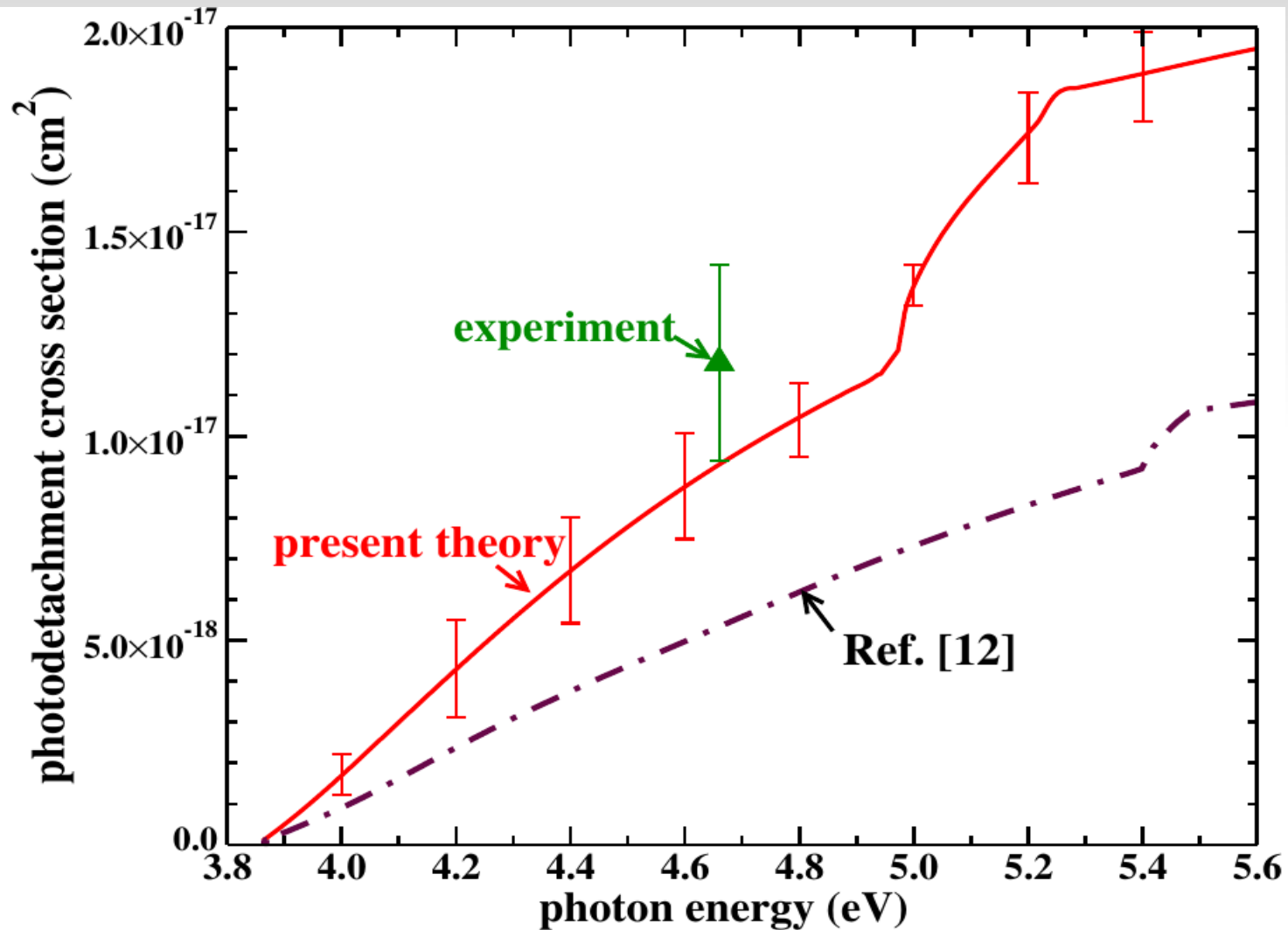
Two different basis sets used: 6-311\* and 6-31\*

# Example 2: Photodetachment of $\text{CN}^-$

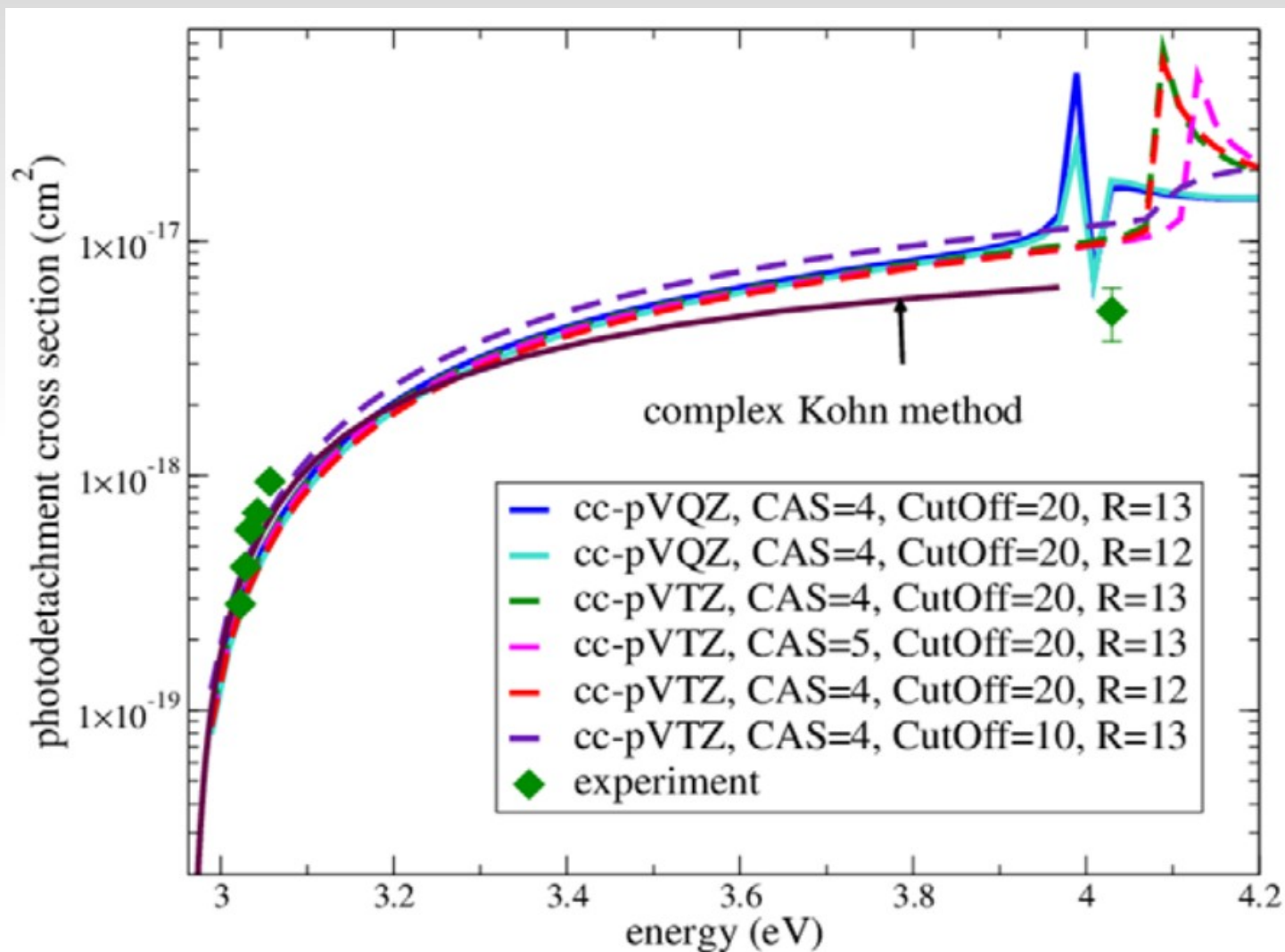
Theoretical results are sensitive to certain parameters in the model. Here, the dependence of the PD cross section is assessed in a qualitative way. The parameters of the model is the (1) basis set, (2) orbital space, (3) the size of the R-matrix box.



# Photodetachment of $\text{CN}^-$

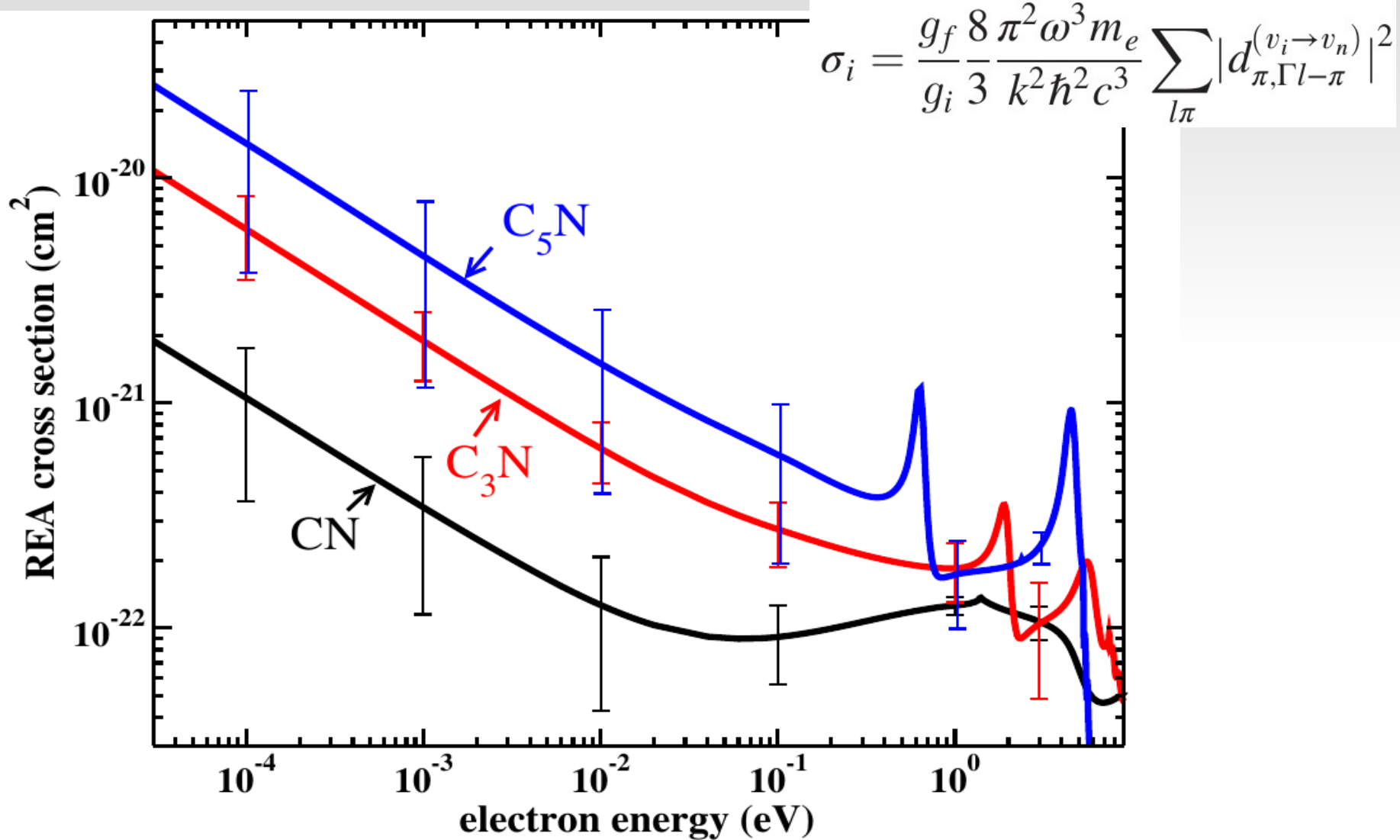


# Photodetachment of $C_2H^-$



# Radiative electron attachment

Larger uncertainty at low electron energies.



# More systematic approach

- \* Advantages: Not-biased, UQ protocol could be established, can be automated
- \* Much more expensive computationally
- \* Could be needed for high-value data

# Mean value and uncertainty

1. The mean value. For example, calculating (measuring)  $\sigma$  at energy  $E_i$

$$\langle \sigma_i \rangle = \int \sigma_i P(\sigma_i) d\sigma_i$$

In theoretical calculations, some of theoretical parameters  $p_j$  are described by similar formulas. For example, if a potential energy surface on  $j=1, N_{\text{pes}}$  grid point is used, it introduces  $N_{\text{pes}}$  parameters  $p_j$ , each having its own uncertainty.

2. Strictly speaking, one has to calculate an  $N$ -dimensional integral if there are several variables:

$$\langle p_j \rangle = \int p_j P(p_1, p_2, \dots, p_j, \dots) d\vec{p}$$

3. Uncertainty (standard deviation)  $\langle \sigma_i \rangle = \int \sigma_i P(\sigma_1, \sigma_2, \dots, \sigma_i, \dots) d\vec{\sigma}$

$$\Delta \sigma_i = \sqrt{\langle (\sigma_i - \langle \sigma_i \rangle)^2 \rangle} = \sqrt{\langle \sigma_i^2 \rangle - \langle \sigma_i \rangle^2}$$

# Covariance matrix and uncertainty

1. *Covariance matrix* describes correlation between variables: Changing a parameter in a model (in the experiment) changes cross sections at all energy points.

$$V_{ii'} = \langle (\sigma_i - \langle \sigma_i \rangle) (\sigma_{i'} - \langle \sigma_{i'} \rangle) \rangle = \langle \sigma_i \sigma_{i'} \rangle - \langle \sigma_i \rangle \langle \sigma_{i'} \rangle$$

2. When  $i=i'$  :

$$V_{ii} = (\Delta \sigma_i)^2$$

it is *variance*.



# Procedure of determination of theoretical uncertainties and evaluated cross sections

1. Choice of the energy grid,  $E_i$  ( $i=1,\dots,N$ ): For evaluation, the grid should be the same as in experiment.
2. Varying parameters within an interval of a few  $\Delta p_j$ , and calculating  $\sigma_i^k$  for each set  $k$  of parameters. Then averaging over  $p$  (summation over  $k$ ) is performed: mean values  $\langle \sigma_i \rangle$  and covariance matrix are obtained

$$\langle \sigma_i \rangle = \int \sigma_i P(p_1, p_2, \dots, p_j, \dots) d\vec{p}$$

$$V_{ii'}^{the} = \langle \sigma_i \sigma_{i'} \rangle - \langle \sigma_i \rangle \langle \sigma_{i'} \rangle = \int \sigma_i \sigma_{i'} P(p_1, p_2, \dots, p_j, \dots) d\vec{p} - \langle \sigma_i \rangle \langle \sigma_{i'} \rangle$$

# Taking into account experimental data

1. Experimental data and uncertainties are needed. The most likely, the covariance matrix  $V_{exp}$  is unknown. Uncertainties should be used to construct diagonal  $V_{exp}$ .

2. One should use a statistical approach again because number of variables ( $\sigma_i$ ) are now determined by the number of grid points.

Now  $\sigma_i^k = \langle \sigma_i \rangle + (2\gamma - 1) \psi \sqrt{V_{ii}^{the}}$  i.e.  $\sigma_i$  is in the interval  $\langle \sigma_i \rangle \pm \gamma \Delta \sigma_i$ .

3. Then, the mean value and covariance matrix are

$$\langle \sigma_i^{eva} \rangle = \frac{\sum_k \sigma_i P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})}{\sum_k P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})};$$

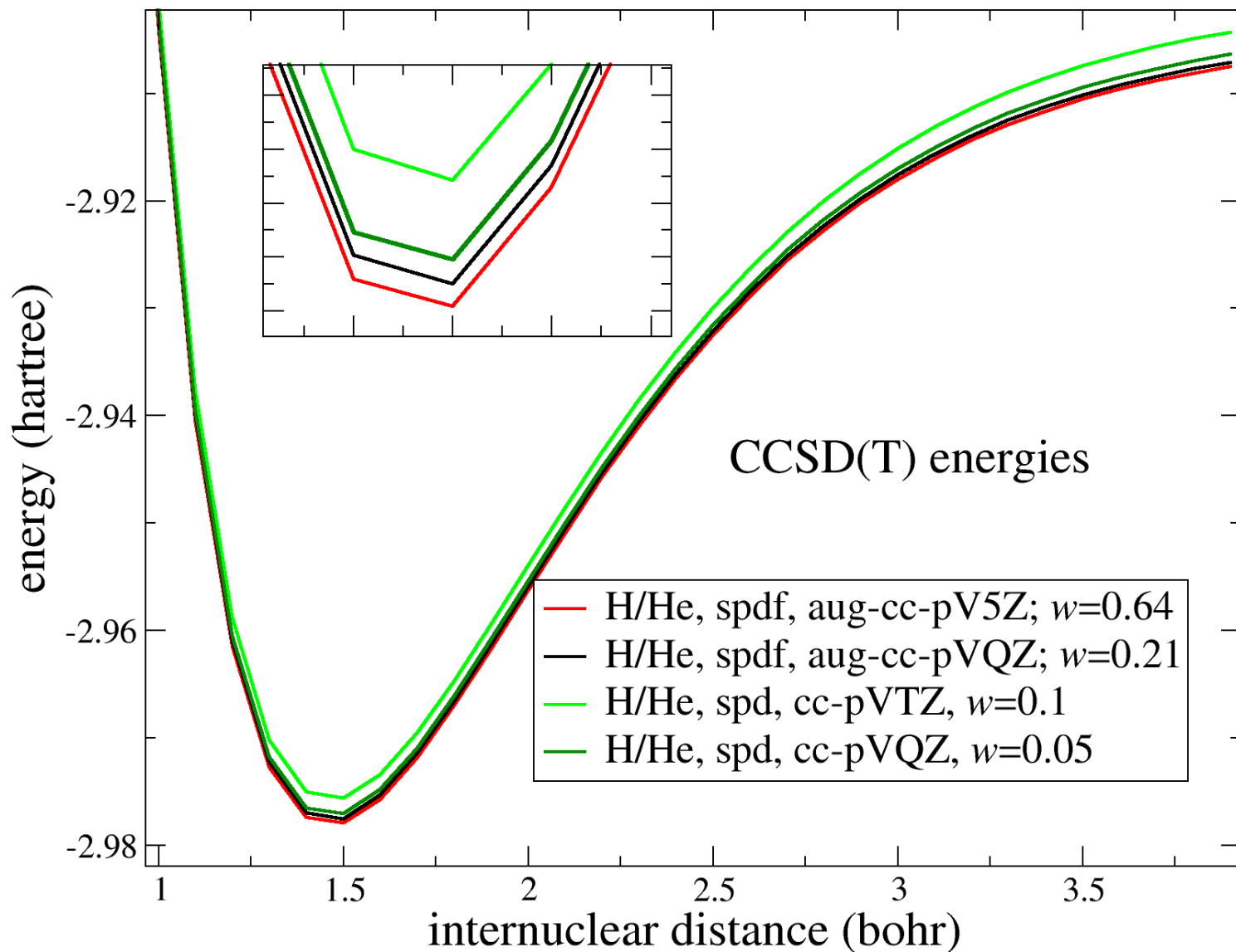
$$\langle \sigma_i^{eva} \sigma_{i'}^{eva} \rangle = \frac{\sum_k \sigma_i \sigma_{i'} P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})}{\sum_k P_{exp}(\vec{\sigma}) P_{the}(\vec{\sigma})}$$

$$V_{ii'}^{eva} = \langle \sigma_i^{eva} \sigma_{i'}^{eva} \rangle - \langle \sigma_i^{eva} \rangle \langle \sigma_{i'}^{eva} \rangle$$

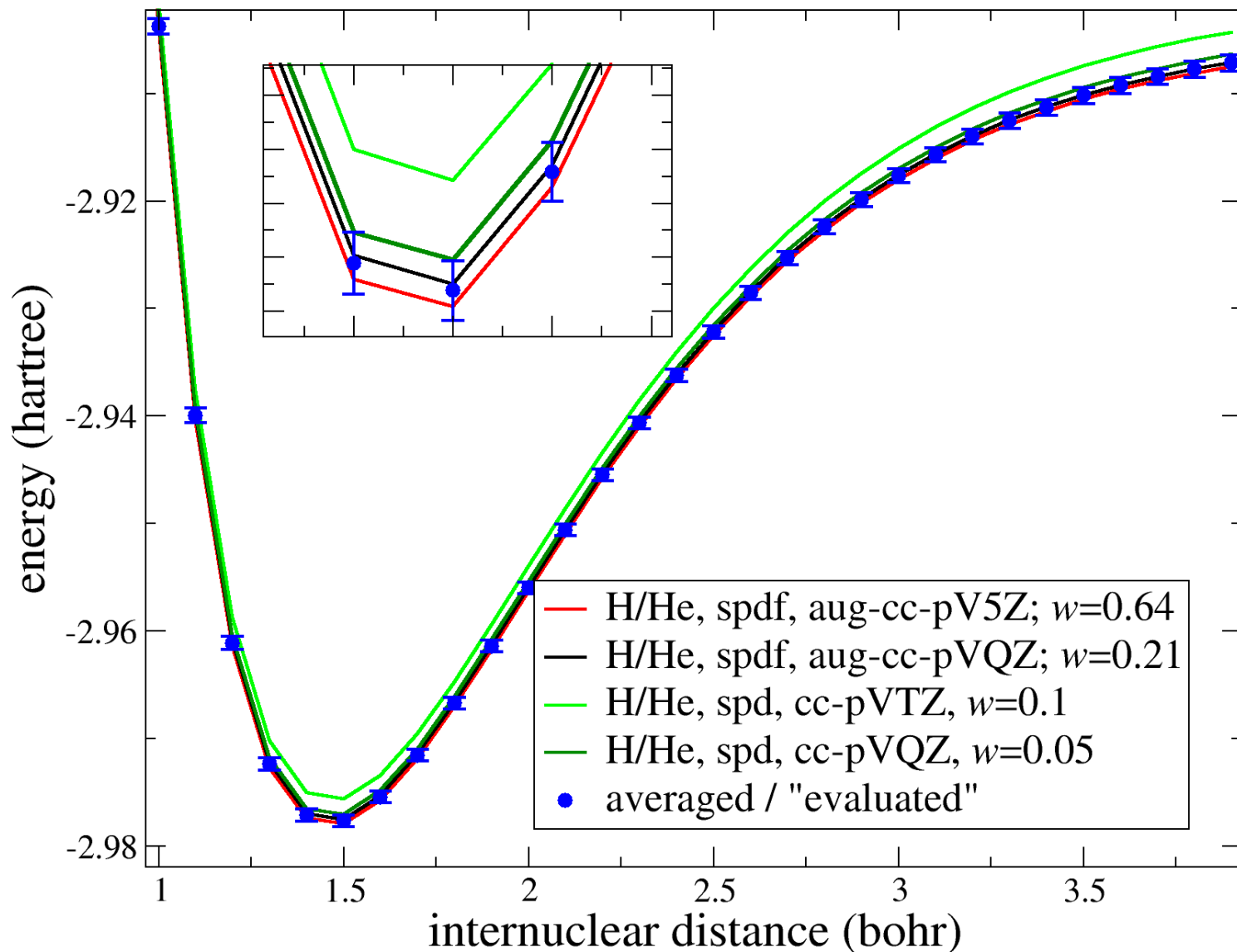
$$P_{the}(\vec{\sigma}) = \exp \left\{ -\frac{1}{2} [(\vec{\sigma} - \vec{\sigma}^{the}) (\hat{V}^{the})^{-1} (\vec{\sigma} - \vec{\sigma}^{the})] \right\}$$

$$P_{exp}(\vec{\sigma}) = \exp \left\{ -\frac{1}{2} [(\vec{\sigma} - \vec{\sigma}^{exp}) (\hat{V}^{exp})^{-1} (\vec{\sigma} - \vec{\sigma}^{exp})] \right\}$$

# Example of systematic approach: HeH<sup>+</sup>



# Uncertainties in HeH<sup>+</sup> PES



# PES variance matrix

0.6277E-06	0.5766E-06	0.5333E-06	0.4979E-06	0.4708E-06	0.4514E-06	0.4382E-06	0.4296E-06	0.4246E-06
0.5766E-06	0.5298E-06	0.4901E-06	0.4577E-06	0.4328E-06	0.4150E-06	0.4029E-06	0.3950E-06	0.3903E-06
0.5333E-06	0.4901E-06	0.4537E-06	0.4238E-06	0.4010E-06	0.3845E-06	0.3733E-06	0.3660E-06	0.3617E-06
0.4979E-06	0.4577E-06	0.4238E-06	0.3962E-06	0.3749E-06	0.3597E-06	0.3492E-06	0.3424E-06	0.3385E-06
0.4708E-06	0.4328E-06	0.4010E-06	0.3749E-06	0.3549E-06	0.3406E-06	0.3308E-06	0.3244E-06	0.3207E-06
0.4514E-06	0.4150E-06	0.3845E-06	0.3597E-06	0.3406E-06	0.3269E-06	0.3176E-06	0.3115E-06	0.3080E-06
0.4382E-06	0.4029E-06	0.3733E-06	0.3492E-06	0.3308E-06	0.3176E-06	0.3085E-06	0.3027E-06	0.2993E-06
0.4296E-06	0.3950E-06	0.3660E-06	0.3424E-06	0.3244E-06	0.3115E-06	0.3027E-06	0.2970E-06	0.2937E-06
0.4246E-06	0.3903E-06	0.3617E-06	0.3385E-06	0.3207E-06	0.3080E-06	0.2993E-06	0.2937E-06	0.2905E-06
0.4226E-06	0.3886E-06	0.3601E-06	0.3370E-06	0.3193E-06	0.3067E-06	0.2981E-06	0.2925E-06	0.2894E-06
0.4235E-06	0.3894E-06	0.3609E-06	0.3377E-06	0.3201E-06	0.3074E-06	0.2988E-06	0.2933E-06	0.2901E-06
0.4268E-06	0.3924E-06	0.3638E-06	0.3405E-06	0.3227E-06	0.3099E-06	0.3013E-06	0.2957E-06	0.2925E-06
0.4321E-06	0.3974E-06	0.3684E-06	0.3448E-06	0.3268E-06	0.3139E-06	0.3051E-06	0.2995E-06	0.2962E-06
0.4390E-06	0.4037E-06	0.3743E-06	0.3504E-06	0.3321E-06	0.3190E-06	0.3101E-06	0.3043E-06	0.3010E-06
0.4470E-06	0.4111E-06	0.3812E-06	0.3569E-06	0.3383E-06	0.3249E-06	0.3158E-06	0.3099E-06	0.3066E-06
0.4558E-06	0.4192E-06	0.3888E-06	0.3640E-06	0.3450E-06	0.3314E-06	0.3221E-06	0.3161E-06	0.3127E-06
0.4651E-06	0.4278E-06	0.3968E-06	0.3716E-06	0.3522E-06	0.3384E-06	0.3289E-06	0.3227E-06	0.3192E-06
0.4750E-06	0.4369E-06	0.4053E-06	0.3795E-06	0.3598E-06	0.3456E-06	0.3359E-06	0.3296E-06	0.3260E-06
0.4852E-06	0.4463E-06	0.4141E-06	0.3879E-06	0.3677E-06	0.3532E-06	0.3433E-06	0.3369E-06	0.3332E-06
0.4958E-06	0.4561E-06	0.4232E-06	0.3965E-06	0.3759E-06	0.3611E-06	0.3510E-06	0.3444E-06	0.3406E-06
0.5067E-06	0.4662E-06	0.4326E-06	0.4053E-06	0.3843E-06	0.3692E-06	0.3588E-06	0.3521E-06	0.3483E-06
0.5178E-06	0.4764E-06	0.4422E-06	0.4143E-06	0.3929E-06	0.3774E-06	0.3668E-06	0.3600E-06	0.3560E-06

\*Large non-diagonal elements.

\*It simply means that points of PES are strongly correlated.

# bound energies variance matrix

v=0	-0.297064691106E+01	0.560088172692E-03	0.290953972746E+04
v=1	-0.295739007263E+01	0.561259572564E-03	0.259982264969E+04
v=2	-0.294554440904E+01	0.566254665879E-03	0.228686761951E+04
v=3	-0.293512467348E+01	0.575567940002E-03	0.196860433847E+04
v=4	-0.292615505214E+01	0.589842246272E-03	0.000000000000E+00

0.3137E-06	0.3143E-06	0.3171E-06	0.3223E-06	0.3303E-06
0.3143E-06	0.3150E-06	0.3178E-06	0.3230E-06	0.3310E-06
0.3171E-06	0.3178E-06	0.3206E-06	0.3259E-06	0.3340E-06
0.3223E-06	0.3230E-06	0.3259E-06	0.3313E-06	0.3395E-06
0.3303E-06	0.3310E-06	0.3340E-06	0.3395E-06	0.3479E-06

\*Large non-diagonal elements (comparable to diagonal elements).

\*It means that points of PES are strongly correlated.

# Concluding remarks

- \*Uncertainty quantification in theoretical calculations (even in *ab initio*) is possible.
- \*Theorists should provide uncertainties.
- \*Different approaches in uncertainty evaluation are acceptable.
- \*The author of theoretical data should describe the procedure how the uncertainties are evaluated.
- \*The community should develop different approaches for uncertainty evaluations adapted for different theoretical models.
- \*UQ in *ab initio* (and maybe, DFT-type) approaches appears to be an exciting research opportunity for quantum chemists.