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

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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 \((\text{aug})-\text{cc-pVxZ}\) \((x=2,3,\ldots)\).
★ At low electron energies, vibrational motion should be accounted for.
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. $\Delta \sigma / \sigma \sim 2 |\Delta S|/|S|$. 
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$^+$ by an electron impact

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

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

$$S_{\Lambda' \Lambda' \Lambda l}(E_{el}) = \langle \psi_{v'}(R) | S_{\Lambda' \Lambda' \Lambda l}(E_{el}) | \psi_{v}(R) \rangle$$

$$S(R) = (1 + iK(R))(1 - iK(R))^{-1}$$

$$S_{\text{phys}}(E) = S^{oo} - S^{oc} \left[ S^{cc} - e^{-2i\beta(E)} \right]^{-1} S^{co}$$

$$S = \begin{pmatrix} S^{oo} & S^{oc} \\ S^{co} & S^{cc} \end{pmatrix}$$
Cross section

\( v = 1 \rightarrow v' = 0, 2, 3 \)

Two different basis sets used: 6-311* and 6-31*
Example 2: Photodetachment of 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 CN$^-$

![Graph showing photodetachment cross section vs. photon energy.](image)
Photodetachment of $\text{C}_2\text{H}^-$
Radiative electron attachment

Larger uncertainty at low electron energies.

\[
\sigma_i = \frac{g_f}{g_i} \frac{8 \pi^2 \omega^3 m_e}{3 k^2 \hbar^2 c^3} \sum_{l\pi} \left| d_{\pi,\Gamma l-\pi}^{(v_i \rightarrow v_n)} \right|^2
\]
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:

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

3. Uncertainty (standard deviation)

$$\langle \sigma_i \rangle = \int \sigma_i P(\sigma_1, \sigma_2, \ldots, \sigma_i, \ldots) \, d\vec{\sigma}$$

$$\Delta \sigma_i = \sqrt{\langle \sigma_i - \langle \sigma_i \rangle \rangle^2} = \sqrt{\langle \sigma_i^2 \rangle - \langle \sigma_i \rangle^2}$$
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.
1. Choice of the energy grid, $E_i (i=1,...,N)$: 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 $\sigma^k_i$ 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

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

$$V_{ii'}^{the} = \langle \sigma_i \sigma_i' \rangle - \langle \sigma_i \rangle \langle \sigma_i' \rangle = \int \sigma_i \sigma_i' P(p_1, p_2, \cdots, p_j, \cdots) d\vec{p} - \langle \sigma_i \rangle \langle \sigma_i' \rangle$$
Taking into account experimental data

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

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 $<\sigma_i> \pm \gamma \Delta \sigma_i$.

3. Then, the mean value and covariance matrix are

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

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

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

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

$$
P_{\text{exp}}(\vec{\sigma}) = \exp \left\{ -\frac{1}{2} \left[ (\vec{\sigma} - \vec{\sigma}_{\text{exp}}) (\hat{V}_{\text{exp}})^{-1} (\vec{\sigma} - \vec{\sigma}_{\text{exp}}) \right] \right\}
$$
Example of systematic approach: HeH^+
Uncertainties in $\text{HeH}^+$ PES

![Graph showing energy vs. internuclear distance for different basis sets and weights.]

- Red line: $\text{H}/\text{He, spdf, aug-cc-pV5Z;} \ w=0.64$
- Black line: $\text{H}/\text{He, spdf, aug-cc-pVQZ;} \ w=0.21$
- Green line: $\text{H}/\text{He, spd, cc-pVTZ,} \ w=0.1$
- Dashed line: $\text{H}/\text{He, spd, cc-pVQZ,} \ w=0.05$
- Blue dots: averaged / "evaluated"
## 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 | 0.3845E-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 | 0.3845E-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 | 0.3080E-06 | 0.3080E-06 | 0.2993E-06 | 0.2937E-06 | 0.2905E-06 | 0.2937E-06 | 0.2905E-06 | 0.2905E-06 | 0.2905E-06 | 0.2905E-06 | 0.2905E-06 | 0.2905E-06 | 0.2905E-06 | 0.2905E-06 |

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*Large non-diagonal elements.*

*It simply means that points of PES are strongly correlated.*
bound energies variance matrix

<table>
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<tr>
<th>v=0</th>
<th>-0.297064691106E+01</th>
<th>0.560088172692E-03</th>
<th>0.290953972746E+04</th>
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<td>0.196860433847E+04</td>
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<tr>
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<td>0.589842246272E-03</td>
<td>0.000000000000E+00</td>
</tr>
</tbody>
</table>

| 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.