Uncertainty assessment of theoretical data on electron-molecule collisions: Examples of $\text{H}_3^+$ and $\text{CH}_4$

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General procedure for evaluation of theoretical data

- Compilation: the relevant data sets are collected
- Evaluation of data sets: each data set should be evaluated by an expert of the corresponding field
- Uncertainties should be estimated
- Decision about recommended values
- If uncertainties are large or unknown, more work could be needed either by another evaluator or, if the data is poor, new theoretical calculations are needed
Collecting data sources

For a given original publication, one should review the theoretical method used to produce data.

1. Is it considered to be appropriate for the process under consideration and the energy domain?
2. Do the obtained data agree with the known physical laws?
3. Discussion of the previous calculations and experimental results.

There could be several original publications for the same process and that cover the same energy domain. The problem then is to choose the most reliable work.
There could be different cases

1. There exist reliable and non-controversial experimental data and the most advanced theoretical method reproduces the results: The method should be considered as a benchmark (at the time of the evaluation). Such a method could be used to produce data for energy domains and molecules that have not been studied in the experiment.

2. No experiment data: the most advanced method should be chosen as a benchmark. In case if other (“less reliable”) methods produce results different from the benchmark method, the evaluation should argue why the other methods are less reliable. Normally, the original article of the benchmark method should discuss this issue.
3. Experimental data disagree with the “most reliable” theoretical model of the process under consideration. The problem could be in theory, experiment, or both. Assuming that there is a problem in theory, there could be several reasons:

(a) The theoretical model is not appropriate. For example, the model does not take into account the major mechanism of the process.

(b) Errors in theoretical formulas

(c) The calculations did not converge. For example, the basis was not appropriate.

(d) Error in the code

In principle, one can identify (a), (b), and (c) but not (d) if enough detail is given in the original publication. In practice, such an evaluation should be made at the level of a journal referee, i.e. it is hardly possible for an evaluator, who has dozens of articles to assess in a limited time. Publications made by well-established researchers have, normally, lower chances to have (b), (c), and (d).
Different theoretical approaches

1. Born approximation

Bethe 1930

\[ \frac{d\sigma}{d\Omega} = \left( \frac{e^2 m}{\hbar^2} \right)^2 \left( \frac{4 k'}{k q} \right)^4 \left\langle n \left| \sum_a e^{-iqr} \right| 0 \right\rangle^2 d\Omega \]

Advantages: it is relatively easy to implement.

Disadvantages: may not be precise especially at low energies.

The condition of applicability: the velocity of the incident electron should be much larger than the velocity of target electrons, which are (de)excited by the impact.

Because the Born approximation is a perturbation approach (Coulomb interaction is treated as a perturbation), the error of the method can be estimated by calculating the second order term. The most likely, only the authors are able to do it.
If $qa_o << 1$, i.e. $\theta << v_o/v$ ($\theta$ is the scattering angle, $v_o$ is a typical velocity of target electrons), the Born approximation takes the form of a dipolar transition:

\[
\frac{d\sigma_n}{dq} = 8\pi \left( \frac{e}{\hbar \nu} \right)^2 \left( \frac{dq}{q} \right) |\langle n | d_x | 0 \rangle|^2
\]

Transition dipole moments $\langle n | d_x | 0 \rangle$ can be obtained from experiments.

One can calculate the transition dipole moments using quantum chemistry methods and use again the Born approximation formula for small angles $\theta$. 

**Born approximation**
Quantum chemistry methods

At low energies, where the Born approximation is not applicable ($v \lesssim v_0$), another treatment beyond the Born approximation is needed. Depending on the process and the energy range, different methods are used.

One has to take into account electron correlations. Several quantum chemistry methods have been developed

1. UK R-matrix code or Quantemol
2. Complex Kohn method and MESA package

The both packages should be used with a caution because it is very easy to produce erroneous data even having invested a lot of effort. There are several well-established trusted users (and developers) of the codes. The studies published by researchers, who are relatively inexperienced with the codes, should clearly indicate that they were able to produce results for known systems of a similar complexity.

3. Schwinger variational method.

Normally, the authors should set error bar to each of the step in the model.
The wave function representing the electron-neutral scattering, with the neutral target in a state $\Gamma$, is expressed as

$$\Psi_{\Gamma \nu} = \sum_{\Gamma'} \hat{A}(\chi_{\Gamma'} F^+_{\Gamma \Gamma'}) + \sum_j b_j^\Gamma \Theta_j$$

where $\Theta_j$ is the “penetration” term and

$$F^+_{\Gamma \Gamma'} = \sum_{j'} c_{j'}^\Gamma \phi_{j'}(r) + \sum_{l',\nu'} \frac{i}{2} [h_{\nu'}^{-}(k_{\Gamma'} r) \delta_{l\nu \nu'} \delta_{\Gamma \Gamma'} - S_{l\nu l\nu'}^{\Gamma \Gamma'} h_{\nu'}^{+}(k_{\Gamma'} r)] Y_{l\nu'}(\hat{r}) / r$$

and with asymptotic behavior

$$h_{\nu'}^{+}(k_{\Gamma'} r) \to \frac{1}{\sqrt{k_{\Gamma'}}} \exp \left( i \left[ k_{\Gamma'} r - \frac{l' \pi}{2} \right] \right)$$

The calculations are made inside a relatively large (compared to the R-matrix approach) box of electron distances $r$. At the end of the box, a complex absorbing potential is applied.

Accuracy example: the value for zero-point CN affinity of 3.91 eV in good agreement with experimental value of 3.86 eV.

Details for specialists here: cc-pVTZ performing a CAS calculation of 9 natural orbitals of CN computed through a MRCI with all single excitations outside the reference space.
Uncertainty in numerical methods

Quantum-chemistry methods (R-matrix, variational complex Kohn method):

➢ The uncertainty could be assessed by varying different parameters in the basis set, the position of where the numerical solution is matched to the asymptotic solution.

➢ However, the full analysis using the *Unified Monte Carlo Approach* (UMC) is difficult because UMC requires a few hundreds different sets of parameters. It is not possible for quantum-chemistry calculations. It should be possible for cross-section calculations.

➢ The accuracy of the calculation can be estimated if something is known about the system. For example, one can calculate the dissociation energy and compare it with experimental value. This will give an idea about the accuracy.

➢ For quantum-chemistry calculations, the uncertainty analysis should be developed.

➢ For quantum chemistry data, it is difficult to estimate the error bar if the author of the data source did not discuss the convergence tests.

➢ If there is a previous work covering (partially) the same energy or/and geometry domain, the uncertainty assessment is easier to perform.
The assessment of numerical methods (including methods of quantum chemistry) will give the uncertainty within the chosen model of the process. For example, for processes involving non-Born-Oppenheimer couplings, one can choose different models how to include such couplings.

For the same set of ab initio data, different models give different results.

For a given model of the process, the evaluation (ideally done by the authors of the original study) should be able to provide error bar for the approximations used in the model. In certain cases, the error due to the used approximations is larger than the produced values. In many cases of electron-molecule collisions it is difficult to know if all approximations used in a model are appropriate (not too crude).
Uncertainty of two types of theoretical data

Therefore, it is reasonable to separate the theoretical data for processes involving two or more atoms into two parts and provide uncertainties for both of them.

1. Data for fixed nuclear position $R$. This may include potential energy surfaces, electron-molecule scattering matrices, transition dipole moments, non-Born-Oppenheimer couplings, etc. In principle, it is possible (for the authors of original studies) to estimate the uncertainties for these quantities. One example: one can use Infinite basis set extrapolation procedure. Although, such cannot be used by the plasma community, it is important to have an evaluated database for these parameters.

2. These data are used to produce physically-meaningful cross-sections. Varying the ab initio data within their uncertainty intervals can be used to perform UMC on the final cross-sections within a chosen model of the process. In some cases, such calculations are fast, in other cases, there are very long.
How to estimate theoretical error in practice?

➢ One can compare the experimental and theoretical data.
➢ If the experiment data is known to be accurate (at least, in a certain interval of energies), the evaluator can estimate the error bar for the theory (~20% for energies above 0.3 meV).
➢ Ideally, the data producer should give an error estimate independent on the experimental results.
Theoretical approach

➢ Vibrational, rotational, electronic and nuclear spin degrees of freedom are explicitly included into the treatment.
➢ Jahn-Teller (non-Born-Oppenheimer) coupling. It describes $e^{-}\text{H}_3^+$ interaction. Only $p$-wave scattering is included.
➢ All three vibrational coordinates have to be taken into account. Vibrational dynamics of $\text{H}_3^+$ is described using the hyper-spherical treatment. Hyper-radius is treated as a dissociation coordinate.
➢ We construct the scattering matrix for $e^{-}\text{H}_3^+$ scattering using quantum defect theory.
We need the $S$-matrix describing the process: $e^- + \text{H}_3^+(j\text{-state}) \rightarrow e^- + \text{H}_3^+(j'\text{-state})$

It can be written as

$$S_{j'j} = \langle \Phi_{j'} | \hat{S} | \Phi_j \rangle_{\text{all coordinates}}$$

It is calculated using the frame transformation approach (Fano, Chang, Atabek, Jungen, Dill)

For this purpose one needs potential energy surfaces of $\text{H}_3$ and $\text{H}_3^+$, non-adiabatic couplings (from quantum chemistry calculation), and rovibrational states of $\text{H}_3^+$.

We construct a so-called smooth scattering matrix and then use the quantum defect theory to calculate the physical scattering matrix

$S_{j'j}$ can also be used, for example, for photoionization.
Uncertainty considerations from the data producer

We can estimate the error in each step of the treatment.

1. The accuracy of potential energy surfaces is better than 1 cm⁻¹.
2. We use the rigid rotor approximation: some of the H₃ resonances could be shifted by a few dozens of cm⁻¹.
3. How does this translate into accuracy of the resulting DR cross section and thermal rate constant? For the cross section some of the resonances are in a wrong place. The rate coefficient for T>50K is insensitive to exact positions of resonances.
4. The overall value of the cross section (rate coefficient) is determined by the accuracy of the non-adiabatic coupling (10%). In addition, the d-wave is neglected, which introduce an error of a 1%. If we take an overall error Δc 11% in the non-adiabatic coupling c, and because σ~c², we have Δσ~22 %.
Cross-section and rate coefficient for dissociative recombination

Experiments: McCall et al. 2004; Kreckel et al. 2006
In the calculations, the same scattering matrix was used.

The vibrational excitation is governed by the same non-Born-Oppenheimer coupling.

Therefore, the same accuracy $\sim 20\%$ is expected.

For the convenience of using in models we fit numerical results with the formula (scaling law)

$$\alpha_{th}(T) = \sqrt{\frac{2\pi}{kT}} e^{-\frac{\Delta_{v,v}^2}{kT}} P_0$$

Vibrational excitation
Schwinger variational method (McKoy)

Our formulation\textsuperscript{19} for collision problems beyond the static-plus-exchange approximation begins with a projected Lippmann-Schwinger equation

$$P\Psi^{(+)}_m = t S_m + G_p^{(+)} V\Psi^{(+)}_m,$$  \hspace{1cm} (2.1)

where $\Psi^{(+)}_m$ is the total scattering wave function of the $m$th channel with plane-wave plus outgoing-wave boundary condition. $P$ defines the open-channel space in terms of the eigenfunctions of the target Hamiltonian $H_N$,

$$P = \sum_{m=1}^{N_0} |\Phi_m(1,2,\ldots,N)\rangle \langle \Phi_m(1,2,\ldots,N)|$$  \hspace{1cm} (2.2)

and

$$H_N |\Phi_m\rangle = E_m |\Phi_m\rangle, \quad E - E_m > 0.$$  \hspace{1cm} (2.3)

The free-particle solution $S_m$ of the unperturbed Hamiltonian $H_0 = H_N + T_{N+1}$ is

$$S_m = \Phi_m e^{i \vec{k}_m \cdot \vec{r}_{N+1}}.$$  \hspace{1cm} (2.4)

The coefficient $t$ associated with $S_m$ is explicitly included to remind us that the antisymmetrizer for $\Psi^{(+)}_m$ is

$$\mathcal{A}_{N+1} = \frac{1}{\sqrt{(N+1)!}} \sum \epsilon_q Q$$  \hspace{1cm} (2.5a)

but for $\Phi_m$ it is

$$\mathcal{A}_N = \frac{1}{\sqrt{N!}} \sum \epsilon_q Q,$$  \hspace{1cm} (2.5b)

and hence

$$t = \frac{1}{\sqrt{N+1}}.$$  \hspace{1cm} (2.6)

The interaction potential $V$ is

$$V = H_{N+1} - H_0 = \sum_{i=1}^{N} \frac{1}{r_{i,N+1}} - \sum_{\alpha} \frac{Z_{\alpha}}{r_{\alpha,N+1}},$$  \hspace{1cm} (2.7)

where the first term on the right-hand side (rhs) represents the electron repulsion and the second term represents the electron-nuclear attraction. The outgoing-wave Green's function $G_p^{(+)}$, which is defined only in the open-channel space ($P$), is

$$G_p^{(+)} = \sum_{m=1}^{N_0} |\Phi_m\rangle g^{(+)}_m(\vec{r}_{N+1},\vec{r}'_{N+1}) \langle \Phi_m|$$ \hspace{1cm} (2.8)

with

$$g^{(+)}_m(\vec{r},\vec{r}') = -\frac{1}{2\pi} \frac{e^{ik_m|\vec{r} - \vec{r}'|}}{|\vec{r} - \vec{r}'|}.$$  \hspace{1cm} (2.9)
Schwinger variational method for e⁻+CH₄

The problem is then reformulated in terms of a functional, where the scattering wave function is expanded in a basis of (N+1)-particle Slater determinants. The coefficients of this expansion are then variationally determined. Pseudo-potentials were employed for e⁻+CH₄. The electronic excitation from the ground $^1A_1$ to an excited $^3T_2$ state is calculated for the equilibrium geometry of the ground state of CH₄.

Lima et al. 1993, re-evaluated in 1998 by authors as not converged although it used a larger basis

Lima et al. 1993,

Rescigno 1994, complex Kohn

Lima et al. 1998; considered the best
Theoreticians should systematically estimate the error of their calculations. If calculations are multi-step, we should try to assess uncertainties introduced by each step. (Usually, I don't pay attention to the error analysis except checking the convergence, but I will start doing it and hope that my co-authors will not be upset too much about it.)

Referring someone's theoretical work we have to request the authors to write a paragraph about the uncertainty of each step. It would be much more efficient if the data producers assess the uncertainty of their data while preparing the article than by someone else years after.

We should try to do case studies of uncertainties. It would be good if we do such a study for major approaches and major processes. It will allow other people to perform the uncertainty assessment and, hopefully, improve the assessment protocol.