Introduction to covariance analysis technique – in contrast to coincidence analysis

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1. Power of coincidence analysis

- Multiple particles coincidence
- Multiple dimensional measurements

\( i^+ : p_x, p_y, p_z \left( \frac{m}{q} \right) \)
\( e^- : p_x, p_y \)
1. Power of coincidence analysis

Data = \( N(\text{particles}) \)

\[ \text{ToF} \]

= \( N(e) + N(i_1) + N(i_2) + \cdots \)

\[ \text{Differential measurements} \]

= \( N(e, p_x, p_y) + N(i_1, p_x, p_y, p_z) + \cdots \)

\[ \text{Coincidence} \]

= \( N(e, p_x, p_y | i_1) + N(i_1, i_2) + \cdots \)

Abel Inversion

= \( N(e, KE, \theta) + N(i_1, KE, \theta) + \cdots \)

Abel Inversion or other analysis

Electron's \( p_x p_y \) image in coincidence with ion specie 1
1. Power of coincidence analysis

Photoelectron in coincidence with different ions

![Graphs showing relative yield vs. comb position for different ionization states.](image)

Neutral state (AB)

Cationic state (AB+)

Binding Energy

\[ KE_{ele} \]

Photoion correlations arised from multi-ionization

![Images illustrating photoion correlations for different pulse durations.](image)
1. Power of coincidence analysis – coincidence power for covariance price

- Coin vs covar analysis in ion-ion events
- Boost factor = 2days/30mins ≈ 100
1. Power of coincidence analysis – coincidence power for covariance price

- Coin vs covar analysis in ion-ion events
- Boost factor = 2days/30mins ≈ 100
- Intensity scan = 20mins*10 ≈ 3 hrs
- Question: why it seems to work so well?

Based on agreement between coincidence and covariance.
• Coincidence analysis
• Agreement between coincidence and covariance

why?

• Expectation of coincidence (math)
• Constraints in speed
2. Expectation in coincidence analysis

• The yield of \((e, i_1)\) events should follow:

\[
\begin{align*}
    w_{\text{coin}} &= \nu_0 \times f(e, i_1) \times \xi_e \xi_{i_1} \\
    \text{Normalized channel branching ratio} \\
    \text{Detection efficiency for electrons and ions} \\
    \text{Rate of all events}
\end{align*}
\]
2. Expectation in coincidence analysis

• The yield of \((e, i_1)\) events should follow:

\[
\frac{w_{\text{coin}}}{w_{\text{all}}} = \nu_0 \ast f(e, i_1) \ast \xi_e \xi_{i_1}
\]

- Rate of all events
- Detection efficiency for electrons and ions
- Normalized channel branching ratio
2. Expectation in coincidence analysis

• In the exp, the data (ionization event) may fluctuate following Poisson distribution:

<table>
<thead>
<tr>
<th>Shot #</th>
<th>e-</th>
<th>H+</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
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<tr>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

\[
\text{Prob}(n) = (\lambda^n/n!)e^{-\lambda} @ \lambda = 0.5 \\
\text{Prob}(n) = (\lambda^n/n!e^{-\lambda} @ \lambda = 5}
\]
2. Expectation in coincidence analysis

- In reality, there are more fragments (different events) in each shot

<table>
<thead>
<tr>
<th>Shot #</th>
<th>e-</th>
<th>H+</th>
<th>O+</th>
<th>OH+</th>
<th>H2O+</th>
<th>...</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3(1)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>...</td>
</tr>
<tr>
<td>2</td>
<td>1(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>...</td>
</tr>
<tr>
<td>3</td>
<td>1(1)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>...</td>
</tr>
<tr>
<td>4</td>
<td>7(1)</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>5</td>
<td>...</td>
</tr>
<tr>
<td>5</td>
<td>3(0)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
<td>...</td>
</tr>
<tr>
<td>6</td>
<td>9(3)</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>...</td>
</tr>
<tr>
<td>7</td>
<td>7(1)</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>...</td>
</tr>
<tr>
<td>8</td>
<td>7(0)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>7</td>
<td>...</td>
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<td>...</td>
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<td>...</td>
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<td>...</td>
</tr>
</tbody>
</table>
2. Expectation in coincidence analysis

\[ w(M, E) = \text{true} + \text{false} = w^{(t)}(M, E) + w^{(f)}(M, E) \]

- All = true + false
- Event rate -> intermediate \( \nu_0 \)

\[ w^{(t)}(M, E) = f(M) f_M(E) p, \]
\[ p = \xi_i \xi_e \nu_0 e^{-q}, \]
\[ q = \nu_0 (\xi_i + \xi_e - \xi_i \xi_e) \]
2. Expectation in coincidence analysis

\[ w(M, E) = \text{true} + \text{false} = w^{(t)}(M, E) + w^{(f)}(M, E) \]

\[ R_{\text{sys}} = \frac{\text{false}}{\text{all}} = \frac{w^{(f)}(M, E)}{w(M, E)} \]

- All = true + false
- Event rate -> intermediate \( \nu_0 \)
- Sys error -> small \( \nu_0 \)
2. Expectation in coincidence analysis

• Typical acquisition times while keep low sys error:
  • 1. Coincidence for \((e, i)\) takes ~ 1hr
  • 2. Coincidence for \((2e, 2i)\) takes ~ 10 days

• Solutions:
  • 1. Go for higher repetition rate -> 100kHz (currently 1kHz) -> more shots per time
  • 2. Go for clever analysis -> covariance analysis

| Shot # | e- | H+ | O+ | OH+ | H2O+ |...
|--------|----|----|----|-----|------|---
| 1      | 3(1)| 1  | 1  | 0   | 1    |...
| 2      | 1(0)| 0  | 0  | 0   | 1    |...
| 3      | 1(1)| 1  | 0  | 0   | 0    |...
| 4      | 7(1)| 1  | 1  | 0   | 5    |...
| 5      | 3(0)| 0  | 0  | 1   | 2    |...
| 6      | 9(3)| 3  | 0  | 2   | 4    |...
| 7      | 7(1)| 1  | 1  | 2   | 3    |...
| 8      | 7(0)| 0  | 0  | 0   | 7    |...
| ...    | ...| ...| ...| ... | ...   |...
• Coincidence analysis
• Agreement between coincidence and covariance

why?

• Expectation of coincidence (math)
• Constraints in speed

• Expectation of covariance (math)
• Example of ToF-ToF
3. Carry out covariance – brief math Poisson distribution

• For Poisson distribution, the expectation values are:

  \[ P(N) = \frac{\lambda^N}{N!} e^{-\lambda}, P(N = 1) = \lambda e^{-\lambda} \]

  \[ \langle N \rangle = \sum NP(N) = \sum N \times \frac{\lambda^N}{N!} e^{-\lambda} = \lambda \]

  \[ \langle N^2 \rangle = \sum N^2 P(N) = \sum N^2 \times \frac{\lambda^N}{N!} e^{-\lambda} = \lambda^2 + \lambda \]

  \[ \text{Cov}(N, N) = \text{Var}(N) = \langle N^2 \rangle - \langle N \rangle^2 = \lambda \]
3. Carry out covariance – brief math

\[ \text{Cov}(N_M, N_E) = \langle N_M N_E \rangle - \langle N_M \rangle \langle N_E \rangle = P_1 V_0 + \sigma^2 V_0^2 (P_1 + P_2)(P_1 + P_3), \]

\[ P_1 = f(M)f_M(E)\xi_i\xi_e \]

Term proportional to fluctuation. For our laser it is small (~2%).

\[ w^{(1)}(M, E) = f(M)f_M(E) p, \]
\[ p = \xi_i \xi_e V_0 e^{-q}, \]
\[ q = V_0 (\xi_i + \xi_e - \xi_i \xi_e) \]

VS

\[ w_{covar} \]
3. Carry out covariance – simulation

\[ w(M, E) = \text{true} + \text{false} = w^{(t)}(M, E) + w^{(f)}(M, E) \]

\[ R_{\text{sys}} = \frac{\text{false}}{\text{all}} = \frac{w^{(f)}(M, E)}{w(M, E)} \]

- All = true + false
- Event rate \( \nu_0 \) the better!!
- Sys error \( \nu_0 \) large!!
3. Carry out covariance – e.g. ToFToF

\[ Cov(N^a, N^b) = \langle N^{t_1}N^{t_2} \rangle - \langle N^{t_1} \rangle \langle N^{t_2} \rangle \]

\[ i \text{ denotes shot number} \]

\[ = \frac{\Sigma N_i^{t_1}N_i^{t_2}}{Shots} - \frac{\Sigma N_i^{t_1}\Sigma N_i^{t_2} - \Sigma N_i^{t_1}N_i^{t_2}}{Shots(Shots - 1)} \]

\[ = \frac{\Sigma N_i^{t_1}N_i^{t_2}}{Shots - 1} - \frac{\Sigma N_i^{t_1}\Sigma N_i^{t_2}}{Shots(Shots - 1)} \]

\[ \approx \frac{\Sigma N_i^{t_1}N_i^{t_2}}{Shots} - \frac{\Sigma N_i^{t_1}\Sigma N_i^{t_2}}{Shots^2} \]

Goal is to compute these two terms summed over \( i \)
3. Carry out covariance – e.g. ToFToF

Language of computing the fluctuation

\[ \text{Cov}(N^a, N^b) = \langle N^{t_1} N^{t_2} \rangle - \langle N^{t_1} \rangle \langle N^{t_2} \rangle \]

\[ = \frac{\sum N_i^{t_1} N_i^{t_2}}{\text{Shots}} - \frac{\sum N_i^{t_1} \sum N_i^{t_2} - \sum N_i^{t_1} N_i^{t_2}}{\text{Shots} (\text{Shots} - 1)} \]

\[ = \frac{\sum N_i^{t_1} N_i^{t_2}}{\text{Shots} - 1} - \frac{\sum N_i^{t_1} \sum N_i^{t_2}}{\text{Shots} (\text{Shots} - 1)} \]

\[ \approx \frac{\sum N_i^{t_1} N_i^{t_2}}{\text{Shots}} - \frac{\sum N_i^{t_1} \sum N_i^{t_2}}{\text{Shots}^2} \]
3. Carry out covariance – e.g. ToFToF

\[ S_{12} = \frac{\sum N_i^{t1} N_i^{t2}}{\text{Shots}} \quad - \quad S_1 S_2 = \frac{\sum N_i^{t1} \sum N_i^{t2}}{\text{Shots}^2} \]
3. Carry out covariance – e.g. ToFToF

- Diagonal
- Negative

$\text{Cov} > 0$

$\text{Cov} < 0$
3. Carry out covariance – diagonal: $t_1 = t_2 = t$

Also counting identical pairs

An event rate is $\lambda$, produces $k$ fragments that has identical detection efficiency $\eta$:

$$\langle N \rangle = \lambda k \eta$$

$$\text{Cov}(N, N) = \lambda (2C_k^2 \eta^2 + k \eta)$$

Contribution of recounting
3. Carry out covariance – e.g. ToFToF

\[ \text{Cov}(N^a, N^b) - \langle N^a \cap N^b \rangle > 0 \]

- Diagonal
- Negative

\[ \text{Cov}(N^a, N^b) > 0 \]
3. Carry out covariance – e.g. ToFToF

- Diagonal
- Negative

\[ \text{Cov} > 0 \]

\[ \text{Cov} < 0 \]

\( CD_2O \)
3. Carry out covariance – negative parts of covariance

\[ D^+: x-y, x-t, y-t \text{ plots} \]

\[ CO^+, CDO^+, CD_2O^+: x-y, x-t, y-t \text{ plots} \]

- Single ionization dissociation low KE
  - \( p_1 + p_2 = 0 \)
  - \( KE_1:KE_2 = m_2:m_1 \)
- Overlapping hits issue

9/15/2021
3. Carry out covariance – negative parts of covariance

\[ p(N) = \begin{cases} 
1 - p = p_1(0) & N = 0 \\
p = \Sigma_{n \geq 1} p_1(n) & N = 1 
\end{cases} \]

And the related statistics are:

\[ \langle N \rangle = p \]
\[ Cov(N, N) = p(1 - p) \]
\[ Cov(N, N) - \langle N \rangle = -p^2 \]

- Any imaging-centroiding detector will have this problem
• Coincidence analysis
• Agreement between coincidence and covariance

why?

• Expectation of coincidence (math)
• Constraints in speed

• Expectation of covariance (math)
• Example of ToF-ToF

• Other covariance, example of our data \(CD_2O\)
• Related thoughts
4. More about covariance – matrix

- $\text{Cov}(N_{i1}, N_{i2})$

- Matrix of covariance

- $\text{Cov}(N_{i1:t1}, N_{i2:t2})$

- $N_{i1} = \sum_{t1} N_{i1:t1}$

- Other observables like $x, y$

From Wikipedia:

$$K_{XX} = \begin{bmatrix}
E[(X_1 - E[X_1])(X_1 - E[X_1])]
& E[(X_1 - E[X_1])(X_2 - E[X_2])] & \cdots & E[(X_1 - E[X_1])(X_n - E[X_n])]

E[(X_2 - E[X_2])(X_1 - E[X_1])]
& E[(X_2 - E[X_2])(X_2 - E[X_2])] & \cdots & E[(X_2 - E[X_2])(X_n - E[X_n])]

\vdots & \vdots & \ddots & \vdots 

E[(X_n - E[X_n])(X_1 - E[X_1])]
& E[(X_n - E[X_n])(X_2 - E[X_2])] & \cdots & E[(X_n - E[X_n])(X_n - E[X_n])]
\end{bmatrix}$$

The definition above is equivalent to the matrix equality

$$K_{XX} = \text{Cov}(X, X) = E[(X - \mu_X)(X - \mu_X)^T] = E[XX^T] - \mu_X\mu_X^T \quad (i=1)$$
4. More about covariance – momentum correlation

Particle 1 choose $D^+$, look at its $x$ direction
Particle 2 choose $CO^+/DCO^+$, look at its $x$ direction

- $\text{Cov}(N_{D^+}^{x}, N_{CO^+/DCO^+}^{x})$
- Momentum conservation
- Coincidence feature
- Angular distribution

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4. More about covariance – momentum correlation

- \( \text{Cov}(N^{D^+:x}, N^{D^+:x}) \)
- 3-body or 4-body dissociation
- Diagonal missing

Particle 1 choose \( D^+ \), look at its \( x \) direction
Particle 2 choose \( D^+ \), look at its \( x \) direction
4. More about covariance – \( \text{Cov}(N_{xy}, N) \)

- \( p_1 + p_2 = 0 \)
- \( KE_1 : KE_2 = m_2 : m_1 \)
- 2-body dissociation
- Angular distribution (alignment)

\[ \text{Cov}(N^{CO^+/DCO^+}_{xy}, N^{D^+}) \]

Particle 1 choose \( CO^+/DCO^+ \), look at its \( xy \) image
Particle 2 choose \( D^+ \), look at its \( \text{sum yield} \)

\[ \text{Cov}(N^{CO^+/DCO^+}, N^{D^+}_{xy}) \]

Particle 1 choose \( CO^+/DCO^+ \), look at its \text{sum yield} \)
Particle 2 choose \( D^+ \), look at its \( xy \) image
4. More about covariance – 3-body dissociation

- Vague angular distribution
- No clear momentum conservation
- Has to do 3-body covariance

\begin{align*}
\text{Cov}(N^{O+}, N^{D+}:x) \\
\text{Cov}(N^{O+}:xy, N^{D+}) \\
\text{Cov}(N^{O+}, N^{D+:xy}) \\
\text{Cov}(N^{O+:x}, N^{D+:y}) \\
\text{Cov}(N^{O+:t}, N^{D+:t})
\end{align*}
4. More about covariance – compared to coincidence

Coincidence:

\((x, y, t)\) list

preprocess

\((x_1, y_1, t_1; x_2, y_2, t_2)\) list

Further analysis, usually histograms

- Momentum correlation
- Angular distribution
  ...

Covariance:

\((x, y, t)\) list

Specific covariance code

Depending on details, \(~ 10s to 10mins\)

- Momentum correlation
- Angular distribution
  ...

We should be doing covariance 10 years ago! O(∩_∩)O
4. More about covariance – related ideas

• The pressure should be proportional to the event rate so 
\[ \operatorname{Cov}(N_e(t), P) \propto \langle N_e \rangle \]?

• For a pump probe system like UV-VUV, would it be possible if: 
\[ \operatorname{Cov}(N_e(t), I_{UV}I_{VUV}) \propto \langle N_e \rangle \text{ assuming } N_e(t) \propto I_{UV}I_{VUV} \]?

• Use ion counts together with photoelectrons

• Partial covariance may help clean some noise as well
• Thanks for joining. Any thoughts or questions?

Check out our paper:

• Coincidence analysis
• Agreement between coincidence and covariance

why?

• Expectation of coincidence (math)
• Constraints in speed

• Expectation of covariance (math)
• Example of ToF-ToF

Other covariance, example of our data ($CD_2O$)
• Related thoughts

Check out our paper:

Some reading materials

https://journals.aps.org/pra/abstract/10.1103/PhysRevA.89.011401
https://pubs.rsc.org/en/content/articlehtml/2020/fd/d0fd00115e
https://www.nature.com/articles/s42004-020-0320-3
https://journals.aps.org/pra/abstract/10.1103/PhysRevA.89.053418

Mainly focus on the following papers:
Appendix 1: CRATI

Neutral state (AB)

\[ KE_{ele} = n\hbar \nu - I_p - E_{Up} - E_{DSS} \]

Cationic state (AB\(^+\))

Excited cationic state(AB\(^{**}\))

\[ KE'_{ele} = n\hbar \nu - I'_p - E'_{Up} - E'_{DSS} \]

- Deeper orbitals
- Different binding energy
- Hard to be ionized
- Dominated by ground state
- Need differential measurements

Neutral state (AB)
Appendix 3: ToFToF computation

\[
\frac{\sum_{i} N_{i}^{t_{1}} N_{i}^{t_{2}}}{\text{ Shots}}
\]

```matlab
for ii = 1:length(trigindex) - 1
    for jj1 = trigindex(ii):trigindex(ii + 1) - 1
        for jj2 = trigindex(ii):trigindex(ii + 1) - 1
            ToFToF(ToFindexes(jj1),ToFindexes(jj2)) = ToFToF(ToFindexes(jj1),ToFindexes(jj2)) + 1;
        end
    end
end
```
Appendix 4: more poisson

• Poisson distribution and multiple events

• Event n follows Poisson distribution:

\[ P(N_n) = \frac{\lambda_n^{N_n}}{N_n!} e^{-\lambda_n} \]

• Simple calculation shows that, summing up all m events to get everything\( N = N_1 + N_2 + ... + N_m \), N follows:

\[ P(N) = \frac{\lambda^N}{N!} e^{-\lambda} \] where \( \lambda = \lambda_1 + \lambda_2 + ... + \lambda_m \)

• Which tells us that: everything is Poisson style.
Appendix 4: more poisson

• For Poisson distribution, the expectation value is:

\[ < N > = \sum NP(N) = \sum N \times \frac{\lambda^N}{N!} e^{-\lambda} = \lambda \]

• \[ < N^2 > = \sum N^2 P(N) = \sum N^2 \times \frac{\lambda^N}{N!} e^{-\lambda} = \lambda^2 + \lambda \]

• \[ < N^3 > = \sum N^3 P(N) = \sum N^3 \times \frac{\lambda^N}{N!} e^{-\lambda} = \lambda^3 + 3\lambda^2 + \lambda \]

• \[ \sqrt{\text{Var}(N)} = \sqrt{< (N - < N >)^2 >} = \sqrt{< N^2 > - < N >^2} = \sqrt{\lambda} \]

• \[ \frac{<N>}{\sqrt{\text{Var}(N)}} = \sqrt{\lambda} \]
Appendix 4: more poisson

• Another view of the covariance: fluctuation between two particles
• Imagine our detection efficiency is 100% for both ele and ion.
• $\text{Cov}(N_e, N_M) = \text{Cov}(N_{M1} + N_{M2} + \ldots, N_M) = \text{Cov}(N_M, N_M) = N_M$

Expand the sources of electrons: with different ions
Nature of irrelevant events the covariance calculation. Note 1 ionization is not going to generate so many different ions!
Nature of Poisson style distribution
Appendix 4: more poisson

• Another view of the covariance: fluctuation between two particles
• Imagine our detection efficiency is 100% for both ele and ion.
• $\text{Cov}(N_e, N_M) = \text{Cov}(N_{M1} + N_{M2} + \ldots, N_M) = \text{Cov}(N_M, N_M) = N_M$

Note that with the help of $N_M$ the $N_e$ has been filtered out to only include events involve $N_M$!!

• $\text{Cov}(\xi_e N_e, \xi_i N_M) = \ldots = \text{Cov}(\xi_e N_M, \xi_i N_M) = \xi_e \xi_i N_M$
1. Strong of coincidence

• 0. the multiple particle nature of the measurement
• 1. MRATI
• 2. short VS long
• 3. example of covariance to fit coincidence
2. Coincidence expectation

• 1. from intuition
• 2. from real math
• 3. the boundary → acquisition time (stat table) → MRI and covariance
3. Carry out covariance

• 1. covar math brief
• 2. covar expectation plot
• 3. example: ToFToF
4. More about covariance

• 1. different covar (ToFToF, Nnxy, NxNy, betaKER) speed and back to coincidence
• 2. possible covar params/apps – UV with ions or laser intensity
• 3. covar constraints** -- comparison and speed boost math