Supplementary Material

Measuring picosecond excited state lifetimes at synchrotron sources

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1 Study of τ^{relative} as a function of $\delta t_{\max}^{\text{relative}}$

In section 4.1 of the article, we introduce a quick estimation method of τ^{relative} using $\delta t_{\max}^{\text{relative}}$ estimate. Let us name the function f, which gives for each $\delta t_{\max}^{\text{relative}}$ the corresponding τ^{relative}. There is no analytical expression of f as its values depend on $\hat{\eta}_{\mathbf{h}}$. However, some characteristics of f can be derived.
In our analysis we deduce the $\delta t_{\max}^{\text{relative}}$ values for a sampling of τ^{relative}. $\delta t_{\max}^{\text{relative}}$ is obtained by minimization of the function G to satisfy (21) for any selected τ^{relative}

$$G(\delta t_{\max}^{\text{relative}}) = \left(\hat{\eta}_{\mathbf{h}}(\delta t_{\max}^{\text{relative}}, \tau^{\text{relative}}) - \tau^{\text{relative}} \frac{1}{\sqrt{2\pi}} e^{\frac{-\delta t_{\max}^{\text{relative}\,2}}{2}}\right)^2 \qquad \text{(i)}$$

We introduce g, the function which for each τ^{relative} gives $\delta t_{\max}^{\text{relative}}$. The ($\tau^{\text{relative}}$, $\delta t_{\max}^{\text{relative}}$) pairs are used to plot g in the interval $]0, +\infty[$.
The curve in (Fig. 1) shows that g is continuous and can be differentiated. Moreover, we note, for all $\tau^{\text{relative}} \in]0, +\infty[$, $\delta t_{\max}^{\text{relative}} < \tau^{\text{relative}}$.
The following relation between τ^{relative} and $\delta t_{\max}^{\text{relative}}$ can be derived from equations (15) and (21).

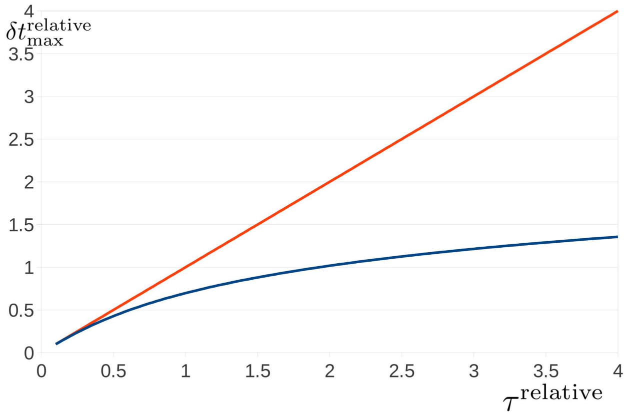
$$\left(\int_{y=U}^{+\infty} e^{-y^2} dy\right) e^{U^2} = \frac{\tau^{\text{relative}}}{\sqrt{2}} \quad \text{with} \quad U = \frac{1}{\sqrt{2}}\left(\frac{1}{\tau^{\text{relative}}} - \delta t_{\max}^{\text{relative}}\right) \qquad \text{(ii)}$$

Differentiating (ii) as a function of τ^{relative} gives the following differential equation

$$g'(\tau^{\text{relative}}) = \frac{1}{\tau^{\text{relative}}}\left(\frac{1}{g(\tau^{\text{relative}})} - \frac{1}{\tau^{\text{relative}}}\right) \qquad \text{(iii)}$$

We notice that $g(\tau^{\text{relative}}) < \tau^{\text{relative}}$ implies $g'(\tau^{\text{relative}}) > 0$, for all $\tau^{\text{relative}} \in]0, +\infty[$. Thus, g is monotonically increasing and reversible, and $f = g^{-1}$ exists. To the best of our knowledge this non-linear first-order differential equation can not be solved. Nevertheless, (ii) and (iii) can be used to study f behavior at $+\infty$ and 0^+.

Figure 1: Plot of τ^{relative} vs. $\delta t_{\text{max}}^{\text{relative}}$. The orange straight line corresponds to the identity function.



1.1 Asymptotic behavior of f at $+\infty$

We remark that when $\tau \longrightarrow +\infty$, $\hat{\eta}_{\mathbf{h}}$ approaches a cumulative Gaussian probability density function (c.g.f.). A c.g.f. is monotonically increasing with its maximum at $+\infty$. Therefore, when $\tau^{\text{relative}} \longrightarrow +\infty$, $\delta_{\max}^{\text{relative}} \longrightarrow +\infty$.

We want to know the asymptotic behavior of g at $+\infty$ and, by the same way, of its reciprocal function f. There are three possible g asymptotic behaviors when $\tau^{\text{relative}} \longrightarrow +\infty$ [1, 5, 4],
1)$g(\tau^{\text{relative}}) \in \underset{+\infty}{o}(\tau^{\text{relative}})$
2)$g(\tau^{\text{relative}}) \in \underset{+\infty}{\Theta}(\tau^{\text{relative}})$
3)$g(\tau^{\text{relative}}) \in \underset{+\infty}{\omega}(\tau^{\text{relative}})$

1) If we assume $g(\tau^{\text{relative}}) \in \underset{+\infty}{o}(\tau^{\text{relative}})$, which means $g(\tau^{\text{relative}}) \ll \tau^{\text{relative}}$ when $\tau^{\text{relative}} \longrightarrow +\infty$, the differential equation (iii) implies the following relation

$$g(\tau^{\text{relative}})g'(\tau^{\text{relative}}) = \frac{1}{\tau^{\text{relative}}} + \underset{+\infty}{o}\left(\frac{1}{\tau^{\text{relative}}}\right) \tag{iv}$$

and also,

$$2g(\tau^{\text{relative}})g'(\tau^{\text{relative}}) \underset{+\infty}{\sim} \frac{2}{\tau^{\text{relative}}} \tag{v}$$

Let us introduce the following functions defined on $]0;+\infty[$ as

$$F_1(\tau^{\text{relative}}) = g(\tau^{\text{relative}})^2 \quad \text{and} \quad G_1(\tau^{\text{relative}}) = \ln(\tau^{\text{relative}}) \tag{vi}$$

When $\tau^{\text{relative}} \longrightarrow +\infty$, the both functions tend to $+\infty$ and also

$\lim\limits_{+\infty} \frac{F'(\tau^{\text{relative}})}{G'(\tau^{\text{relative}})} = \lim\limits_{+\infty} \frac{g(\tau^{\text{relative}})g'(\tau^{\text{relative}})}{1/\tau^{\text{relative}}} = 1$

Then, we can apply l'Hôpital's rule [2], $\lim\limits_{+\infty} \frac{F'(\tau^{\text{relative}})}{G'(\tau^{\text{relative}})} = \lim\limits_{+\infty} \frac{F(\tau^{\text{relative}})}{G(\tau^{\text{relative}})} = 1$

Therefore, by definition of the equivalence of two functions at $+\infty$,

$$g(\tau^{\text{relative}})^2 \underset{+\infty}{\sim} 2\ln(\tau^{\text{relative}}) \tag{vii}$$

Moreover, the function Square-Root, **sqrt**, defined on $[0, +\infty[$, is monotonic and $\frac{\mathbf{sqrt}'(x)}{\mathbf{sqrt}(x)} = \underset{+\infty}{O}(1/x)$ and we know $g(\tau^{\text{relative}})^2 \underset{+\infty}{\longrightarrow} +\infty$.
We can apply Entringer's theorem [3] and obtain,

$$g(\tau^{\text{relative}}) \underset{+\infty}{\sim} \sqrt{2\ln(\tau^{\text{relative}})} \tag{viii}$$

2) If we assume $g(\tau^{\text{relative}}) \in \Theta(\tau^{\text{relative}})$, g and the identity function share the same order of magnitude at $+\infty$. We already know $g(\tau^{\text{relative}}) < \tau^{\text{relative}}$ and so, by definition of “Big omega”, there is $k_1 \in]0, +\infty[$ such that $k_1\tau^{\text{relative}} \leq g(\tau^{\text{relative}})$ at $+\infty$.
Thus,

$$k_1\tau^{\text{relative}} \leq g(\tau^{\text{relative}}) < \tau^{\text{relative}} \tag{ix}$$

Using the differential equation (iii), we obtain at $+\infty$

$$0 < g'(\tau^{\text{relative}}) \leq \left(\frac{1}{k_1} - 1\right) \frac{1}{\tau^{\text{relative}^2}} \tag{x}$$

This satisfies the definition of “Big omicron” relation,

$$g'(\tau^{\text{relative}}) \in \underset{+\infty}{O}\left(\frac{1}{\tau^{\text{relative}^2}}\right) \tag{xi}$$

We note $\lim\limits_{+\infty} \frac{1}{\tau^{\text{relative}^2}} = 0$, and so $\lim\limits_{+\infty} g'(\tau^{\text{relative}}) = 0$.

Let us define the functions F_2 and G_2 on $]0; +\infty[$ as

$$F_2(\tau^{\text{relative}}) = g(\tau^{\text{relative}}) \quad \text{and} \quad \mathrm{G}_2(\tau^{\text{relative}}) = \tau^{\text{relative}} \tag{xii}$$

We note $F(\tau^{\text{relative}}) \underset{+\infty}{\longrightarrow} +\infty$, $G(\tau^{\text{relative}}) \underset{+\infty}{\longrightarrow} +\infty$ and
$\lim\limits_{+\infty} \frac{F_2'(\tau^{\text{relative}})}{G_2'(\tau^{\text{relative}})} = \lim\limits_{+\infty} g'(\tau^{\text{relative}}) = 0$

If we apply once again l’Hôpital’s rule [2], we obtain
$\lim\limits_{+\infty} \frac{F_2(\tau^{\text{relative}})}{G_2(\tau^{\text{relative}})} = \lim\limits_{+\infty} \frac{F_2'(\tau^{\text{relative}})}{G_2'(\tau^{\text{relative}})} = \lim\limits_{+\infty} g'(\tau^{\text{relative}}) = 0$

This implies F_2 is dominated by G_2 at $+\infty$ or $g(\tau^{\text{relative}}) \in \underset{+\infty}{o}(\tau^{\text{relative}})$.
There is a contradiction with the initial assumption: $g(\tau^{\text{relative}}) \in \underset{+\infty}{\Theta}(\tau^{\text{relative}})$.

3) If we assume $g(\tau^{\text{relative}}) \in \underset{+\infty}{\omega}(\tau^{\text{relative}})$, which means, when $\tau^{\text{relative}} \longrightarrow +\infty$, $g(\tau^{\text{relative}}) \gg \tau^{\text{relative}}$, this implies

$$g'(\tau^{\text{relative}}) = -\frac{1}{\tau^{\text{relative}^2}} + \underset{+\infty}{o}\left(\frac{1}{\tau^{\text{relative}^2}}\right) \tag{xiii}$$

and

$$g'(\tau^{\text{relative}}) = \underset{+\infty}{O}\left(\frac{1}{\tau^{\text{relative}^2}}\right) \tag{xiv}$$

Using the same functions than in the previous case, we obtain a contradiction with the initial assumption.

Finally, the only possible behavior is the first one, $g(\tau^{\text{relative}}) \underset{+\infty}{\sim} \sqrt{\ln(\tau^{\text{relative}^2})}$.

More information can be obtained using Gauss error function properties.
We know $\delta_{\max}^{\text{relative}} \underset{+\infty}{\longrightarrow} +\infty$ and $U \underset{+\infty}{\longrightarrow} -\infty$ (ii).
The complementary Gauss error function, noted **erfc**, is defined as

$$\mathbf{erfc}(x) = 1 - \mathbf{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{y=x}^{+\infty} e^{-y^2} dy \tag{xv}$$

and its asymptotic expansion at $+\infty$ is known

$$\sqrt{\pi} x e^{x^2} \mathbf{erfc}(x) \underset{+\infty}{\sim} 1 + \sum_{m=1}^{+\infty} \frac{(-1)^m (2m-1)!!}{(2x^2)^m} \tag{xvi}$$

So, at the zero order,

$$\sqrt{\pi} x e^{x^2} \mathbf{erfc}(x) \underset{+\infty}{\sim} 1 \tag{xvii}$$

Moreover,

$$\mathbf{erfc}(-x) = 1 - \mathbf{erf}(-x) = 1 + \mathbf{erf}(x) = 2 - \mathbf{erfc}(x) \tag{xviii}$$

Therefore,

$$\begin{aligned}
\left(\int_{y=U}^{+\infty} e^{-y^2} dy\right) e^{U^2} &= \frac{\sqrt{\pi}}{2}\left[2 - \int_{y=-U}^{+\infty} e^{-y^2} dy\right] e^{U^2} \\
&= \sqrt{\pi} e^{U^2} - \frac{\sqrt{\pi}}{2}\left(\int_{y=-U}^{+\infty} e^{-y^2} dy\right) e^{U^2} \\
&= \sqrt{\pi} e^{U^2} - \frac{\sqrt{\pi}}{2}\left(\frac{1}{\sqrt{\pi}(-U)}\right) + \underset{+\infty}{O}\left(\frac{1}{U^3}\right) \\
&\underset{+\infty}{\sim} \sqrt{\pi} e^{U^2}
\end{aligned} \tag{xix}$$

We can expand the exponential factor, using the expression of U (ii),

$$\sqrt{\pi} e^{U^2} = \sqrt{\pi}\left[e^{\left(\frac{1}{2\tau^{\text{relative}2}}\right)} e^{\left(\frac{\delta t_{\max}^{\text{relative}2}}{2}\right)} e^{\left(\frac{\delta t_{\max}^{\text{relative}}}{\tau^{\text{relative}}}\right)}\right] \tag{xx}$$

We know $\frac{1}{2\tau^2} \underset{+\infty}{\longrightarrow} 0$ and the asymptotic behavior of $\delta t_{\max}^{\text{relative}}$,
$\frac{\delta t_{\max}^{\text{relative}}}{\tau^{\text{relative}}} \underset{+\infty}{\sim} \frac{\sqrt{\ln(\tau^{\text{relative}2})}}{\tau^{\text{relative}}} \underset{+\infty}{\longrightarrow} 0$
Thus,

$$\sqrt{\pi} e^{U^2} \underset{+\infty}{\sim} \sqrt{\pi} e^{\left(\frac{\delta t_{\max}^{\text{relative}2}}{2}\right)} \tag{xxi}$$

Using (ii), (xix) and (xxi), we obtain the following equation when $\tau^{\text{relative}} \longrightarrow +\infty$

$$\tau^{\text{relative}} \underset{+\infty}{\sim} \sqrt{2\pi} e^{\left(\frac{\delta t_{\max}^{\text{relative}2}}{2}\right)} \tag{xxii}$$

and, by the same way, the asymptotic behavior of f when $\delta t_{\max}^{\text{relative}} \longrightarrow +\infty$

$$f(\delta t_{\max}^{\text{relative}}) \underset{+\infty}{\sim} \sqrt{2\pi} e^{\left(\frac{\delta t_{\max}^{\text{relative}\,2}}{2}\right)} \tag{xxiii}$$

1.2 Asymptotic behavior of f at 0^+

In section 2.1 of the article, we show $\hat{\eta}_{\mathbf{h}}$ is related to an Exponentially Modified Gaussian, E.M.G. For $\delta t^{\text{relative}} \in]-\infty, +\infty[$,

$$\hat{\eta}_{\mathbf{h}}(\delta t^{\text{relative}}) = K_{\mathbf{h}} \tau^{\text{relative}} \mathbf{EMG}(\delta t^{\text{relative}}) \tag{xxiv}$$

Considering the expression (xxiv), for all $\tau_{\text{relative}} \in]0, +\infty[$, $\hat{\eta}_{\mathbf{h}}$ and $\mathbf{EMG}$ share the same maximum location $\delta t_{\max}^{\text{relative}}$

$$\delta t_{\max}^{\text{relative}}{}_{\hat{\eta}_{\mathbf{h}}} = \delta t_{\max}^{\text{relative}}{}_{\mathbf{EMG}} \tag{xxv}$$

Moreover, when $\tau^{\text{relative}} = 0$, an E.M.G. function becomes a Gaussian function, while $\delta t_{\max}^{\text{relative}}{}_{\hat{\eta}_{\mathbf{h}}}$ is a constant function set to zero and consequently has no maximum.
By continuity, $\delta t_{\max}^{\text{relative}}{}_{\hat{\eta}_{\mathbf{h}}}(0^+)$ can be computed

$$\lim_{0^+} \delta t_{\max}^{\text{relative}}{}_{\hat{\eta}_{\mathbf{h}}}(\tau^{\text{relative}}) = \lim_{0^+} \delta t_{\max}^{\text{relative}}{}_{\mathbf{EMG}}(\tau^{\text{relative}}) = \delta t_{\max}^{\text{relative}}{}_{\mathbf{EMG}}(0) = 0 \tag{xxvi}$$

The behavior of g at 0^+ can be studied using the same method than at $+\infty$. There are three possibilities of behavior [1, 5, 4].

1) $g(\tau^{\text{relative}}) = \underset{0^+}{o}(\tau^{\text{relative}})$ which means $g(\tau^{\text{relative}}) \ll \tau^{\text{relative}}$ when $\tau^{\text{relative}} \longrightarrow 0^+$, this implies considering equation (iii)

$$2g(\tau^{\text{relative}})g'(\tau^{\text{relative}}) - \frac{2}{\tau^{\text{relative}}} = \underset{0^+}{o}\left(\frac{1}{\tau^{\text{relative}}}\right) \tag{xxvii}$$

Let us define the functions F_3 and G_3 as

$$\begin{aligned} F_3(\tau^{\text{relative}}) =& 2g(\tau^{\text{relative}})^2 - 2\ln(\tau^{\text{relative}}) \\ &\text{and} \\ G_3(\tau^{\text{relative}}) =& \ln(\tau^{\text{relative}}) \end{aligned} \tag{xxviii}$$

When $\tau^{\text{relative}} \longrightarrow 0^+$, $g(\tau^{\text{relative}}) \longrightarrow 0^+$ and so, $F_3(\tau^{\text{relative}}) \longrightarrow +\infty$ and $G_3(\tau^{\text{relative}}) \longrightarrow -\infty$
Moreover, $\lim_{0^+} \frac{F_3'(\tau^{\text{relative}})}{G_3'(\tau^{\text{relative}})} = 0$ and $\lim_{0^+} \frac{F_3(\tau^{\text{relative}})}{G_3(\tau^{\text{relative}})} = -1$

We can apply l'Hôpital's rule [2], which implies $\lim\limits_{0^+}\frac{F_3(\tau^{\text{relative}})}{G_3(\tau^{\text{relative}})} = \lim\limits_{0^+}\frac{F_3'(\tau^{\text{relative}})}{G_3'(\tau^{\text{relative}})}$ which means $0 = -1$. There is a contradiction.

2) $g(\tau^{\text{relative}}) = \underset{0^+}{\omega}(\tau^{\text{relative}})$ which means $g(\tau^{\text{relative}}) \gg \tau^{\text{relative}}$ when $\tau^{\text{relative}} \longrightarrow 0^+$, this implies

$$g'(\tau^{\text{relative}}) + \frac{1}{{\tau^{\text{relative}}}^2} = \underset{0^+}{o}\left(\frac{1}{{\tau^{\text{relative}}}^2}\right) \tag{xxix}$$

Let us introduce the functions F_4 and G_4

$$\begin{aligned} F_4(\tau^{\text{relative}}) =& g(\tau^{\text{relative}}) - \frac{1}{\tau^{\text{relative}}} \\ &\text{and} \\ G_4(\tau^{\text{relative}}) =& -\frac{1}{\tau^{\text{relative}}} \end{aligned} \tag{xxx}$$

When $\tau^{\text{relative}} \longrightarrow 0^+$, $g(\tau^{\text{relative}}) \longrightarrow 0^+$ and so, $F_4(\tau^{\text{relative}}) \longrightarrow -\infty$ and $G_4(\tau^{\text{relative}}) \longrightarrow -\infty$

Moreover, $\lim\limits_{0^+}\frac{F_4'(\tau^{\text{relative}})}{G_4'(\tau^{\text{relative}})} = 0$ and $\lim\limits_{0^+}\frac{F_4(\tau^{\text{relative}})}{G_4(\tau^{\text{relative}})} = 1$

Using l'Hôpital's rule [2], the both limits should be equal. There is a contradiction again.

3) The only possible behavior is $g(\tau^{\text{relative}}) \in \Theta(\tau^{\text{relative}})$

When $\tau^{\text{relative}} \longrightarrow 0^+$, g has the order of magnitude than the identity function.

Like at $+\infty$, an equivalence relation for $\delta t_{\max}^{\text{relative}}$ can be obtained at 0^+.

When $\tau^{\text{relative}} \longrightarrow 0^+$, $\delta t_{\max}^{\text{relative}} \longrightarrow 0^+$ and $U \longrightarrow +\infty$.

Therefore, when $\tau^{\text{relative}} \longrightarrow 0^+$,

$$\begin{aligned} \left(\int_{y=U}^{+\infty} e^{-y^2}dy\right)e^{U^2} =& \frac{\sqrt{\pi}}{2}e^{U^2}\mathbf{erfc}(U) \\ =& \frac{\sqrt{\pi}}{2}\left(\frac{1}{\sqrt{\pi}U}\right)\left[1 - \frac{1}{2U^2} + \underset{0^+}{o}\left(\frac{1}{U^3}\right)\right] \end{aligned} \tag{xxxi}$$

We show previously, $\delta t_{\max}^{\text{relative}} \in \underset{0^+}{\Theta}(\tau^{\text{relative}})$ at 0^+. The Taylor expansion of the function $\tau^{\text{relative}} \longrightarrow U^{-1}$ can be done relatively to τ^{relative} and $\delta t_{\max}^{\text{relative}}$, which share the same order of magnitude.

$$\frac{1}{U} = \sqrt{2}\tau^{\text{relative}}\sum_{k=0}^{\infty}(\tau^{\text{relative}}\delta t_{\max}^{\text{relative}})^k \tag{xxxii}$$

$$\frac{1}{U} = \sqrt{2}\tau^{\text{relative}}\left(1 + \tau^{\text{relative}}\delta t_{\max}^{\text{relative}}\right) + O((\tau^{\text{relative}}; \delta t_{\max}^{\text{relative}})^4) \qquad \text{(xxxiii)}$$

Note: $O((\tau^{\text{relative}}; \delta t_{\max}^{\text{relative}})^4)$ means the function can be any ones defined as: $\tau^{\text{relative}} \longrightarrow {\tau^{\text{relative}}}^k {\delta t_{\max}^{\text{relative}}}^{4-k}$ with $k \in [0, 1, 2, 3, 4]$.

Then, the expansion (xxxi) becomes

$$\left(\int_{y=U}^{+\infty} e^{-y^2} dy\right) e^{U^2} = \frac{1}{\sqrt{2}}\left(\tau^{\text{relative}} + {\tau^{\text{relative}}}^2 \delta t_{\max}^{\text{relative}} - {\tau^{\text{relative}}}^3\right) + O((\tau^{\text{relative}}; \delta t_{\max}^{\text{relative}})^4) \qquad \text{(xxxiv)}$$

which gives using the relation (ii),

$$\frac{\tau^{\text{relative}}}{\sqrt{2}} = \frac{1}{\sqrt{2}}\left(\tau^{\text{relative}} + {\tau^{\text{relative}}}^2 \delta t_{\max}^{\text{relative}} - {\tau^{\text{relative}}}^3\right) + O((\tau^{\text{relative}}; \delta t_{\max}^{\text{relative}})^4) \qquad \text{(xxxv)}$$

After reducing the expression, we obtain

$$\tau^{\text{relative}} = \delta t_{\max}^{\text{relative}} + \underset{0^+}{O}((\tau^{\text{relative}}; \delta t_{\max}^{\text{relative}})^2) \qquad \text{(xxxvi)}$$

Finally, when $\tau^{\text{relative}} \longrightarrow 0^+$

$$\tau_{\max}^{\text{relative}} \underset{0^+}{\sim} \delta t_{\max}^{\text{relative}} \qquad \text{(xxxvii)}$$

which implies, when $\delta t_{\max}^{\text{relative}} \longrightarrow 0^+$

$$f(\delta t_{\max}^{\text{relative}}) \underset{0^+}{\sim} \delta t_{\max}^{\text{relative}} \qquad \text{(xxxviii)}$$

References

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