Two-photon Lithography

We pose the question whether two-photon processes can be used to increase the contrast in an imaging process. This is certainly true in a coherent two-photon process via a (virtual) intermdiate state. These processes depend on the square of the field, and hence on the 4th power of the field, or the square of the intensity.
A two-step process can be implemented through the reaction of two species, here called X,Y to generate a third species, Z, in a serial reaction where only the first step (from X to Z) is reversible.
The following equations model the problem.

■ Rate Equations

```
Clear[x, y, z, ka, kb, k, A]
sol = DSolve[{
    x'[t] == y[t] k  - x[t] ka,
    y'[t] == - x'[t] - y[t] k - kb y[t],
    z'[t] == + kb y[t]}, {x[t], y[t], z[t]}, t
  ];
```

■ Solutions

```
x[t_] = x[t] /. sol[[1, 1]];

y[t_] = y[t] /. sol[[1, 2]];

z[t_] = z[t] /. sol[[1, 3]];
```

■ Initial conditions

```
Simplify[x[0]]

C[1]

Simplify[y[0]]

C[2]

Simplify[z[0]]

C[3]

Simplify[x[0] + y[0] + z[0]]

C[1] + C[2] + C[3]
```

Full form of solution

```
Simplify[Expand[x[t]]]
```

$$\left(e^{-\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)t}\left(4\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)k^2\,C[1]+(ka-kb)\left(\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)ka-\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)kb-\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)C[1]+2\,k\left(2\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)kb\,C[1]+\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,(C[1]+C[2])\right)\right)\right)\Big/\left(2\left(4\,k^2+(ka-kb)^2+4\,k\,kb\right)\right)$$

```
Simplify[%]
```

$$\left(e^{-\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)t}\left(4\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)k^2\,C[1]+(ka-kb)\left(\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)ka-\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)kb-\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)C[1]+2\,k\left(2\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)kb\,C[1]+\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,(C[1]+C[2])\right)\right)\right)\Big/\left(2\left(4\,k^2+(ka-kb)^2+4\,k\,kb\right)\right)$$

Set values for initial conditions

```
x[t_] = x[t] /. {C[1] → A, C[2] → 0, C[3] → 0};
y[t_] = y[t] /. {C[1] → A, C[2] → 0, C[3] → 0};
z[t_] = z[t] /. {C[1] → A, C[2] → 0, C[3] → 0};

x[t_] = Simplify[x[t]];
y[t_] = Simplify[y[t]];
z[t_] = Simplify[z[t]];
```

```
x[t]
```

$$\left(A\,e^{-\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)t}\left(4\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)k^2+(ka-kb)\left(\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)ka-\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)kb-\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)+2\,k\left(2\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)kb+\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)\right)\right)\Big/\left(2\left(4\,k^2+(ka-kb)^2+4\,k\,kb\right)\right)$$

```
y[t]
```

$$\left(A\,e^{-\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)t}\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)ka\,\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right)\Big/\left(4\,k^2+(ka-kb)^2+4\,k\,kb\right)$$

```
Simplify[z[t]]
```

$$
\begin{aligned}
-\Bigg(&A\, e^{-\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right) t}\, kb \\
&\Big(4\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right) t}\right) k^2 + \\
&\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right) t}\right) ka^2 + \\
&ka\Big(-2\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right) t}\right) kb + \\
&\quad\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\Big) + \\
&kb\Big(\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right) t}\right) kb + \\
&\quad\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\Big) + \\
&2\,k\Big(2\left(1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(2\,k+ka+kb+\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\right) t}\right) kb + \\
&\quad\left(-1+e^{\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,(k+kb)+(2\,k+ka+kb)^2}\Big)\Big)\Bigg) \Big/ \\
&\left(2\,(k+kb)\left(4\,k^2+(ka-kb)^2+4\,k\,kb\right)\right)
\end{aligned}
$$

■ Numerical Example

```
subs = {ka → 4, kb → 2, k → 0.1}
xx[t_] = x[t] /. subs
yy[t_] = y[t] /. subs
zz[t_] = z[t] /. subs
```

$\{ka \to 4,\ kb \to 2,\ k \to 0.1\}$

$$0.103306\, A\, e^{-4.2\,t}\left(0.04\left(1+e^{2.2\,t}\right)+2\left(-2.2\left(-1+e^{2.2\,t}\right)+2\left(1+e^{2.2\,t}\right)\right)+0.2\left(2.2\left(-1+e^{2.2\,t}\right)+4\left(1+e^{2.2\,t}\right)\right)\right)$$

$$1.81818\, A\, e^{-4.2\,t}\left(-1+e^{2.2\,t}\right)$$

$$
\begin{aligned}
-0.0983865\, A\, e^{-4.2\,t}\Big(&16.04\left(1+e^{2.2\,t}-2\,e^{4.2\,t}\right)+4\left(2.2\left(-1+e^{2.2\,t}\right)-4\left(1+e^{2.2\,t}-2\,e^{4.2\,t}\right)\right) + \\
&2\left(2.2\left(-1+e^{2.2\,t}\right)+2\left(1+e^{2.2\,t}-2\,e^{4.2\,t}\right)\right)+0.2\left(2.2\left(-1+e^{2.2\,t}\right)+4\left(1+e^{2.2\,t}-2\,e^{4.2\,t}\right)\right)\Big)
\end{aligned}
$$

```
xx[t]
```

$$0.103306\, A\, e^{-4.2\,t}\left(0.04\left(1+e^{2.2\,t}\right)+2\left(-2.2\left(-1+e^{2.2\,t}\right)+2\left(1+e^{2.2\,t}\right)\right)+0.2\left(2.2\left(-1+e^{2.2\,t}\right)+4\left(1+e^{2.2\,t}\right)\right)\right)$$

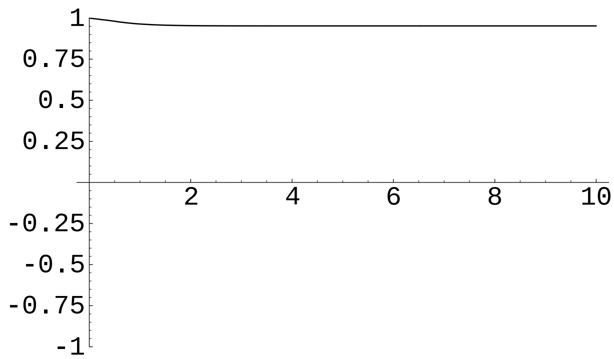
```
A = 1
```

1

```
xx[10] + yy[10] + zz[10]
```

0.952381

```
Plot[xx[t] + yy[t] + zz[t], {t, 0, 10}, PlotRange → {-1, 1}]
```

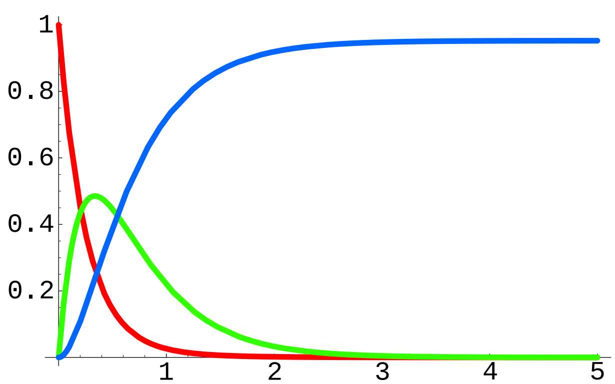


- Graphics -

```
xx[5]
```

4.12796×10^{-6}

```
Plot[{xx[t], yy[t], zz[t]}, {t, 0, 5}, PlotStyle → {{Thickness[0.01], Hue[0.0]},
   {Thickness[0.01], Hue[0.3]}, {Thickness[0.01], Hue[0.6]}}]
```



- Graphics -

■ Stepwise Contrast

We define the contrast at each step:

```
gamma = 0.8
```

■ Limiting case of no decay

```
ClearAll[xx, yy, zz, ka, kb]
```

```
subs = {k → 0}
xx[t_] = x[t] /. subs
yy[t_] = y[t] /. subs
zz[t_] = z[t] /. subs
```

$\{k \to 0\}$

$$\frac{1}{2\,(ka-kb)}\left(e^{-\frac{1}{2}\left(ka+kb+\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)t}\left(\left(1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}\right)ka-\left(1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}\right)kb-\left(-1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)\right)$$

$$\frac{1}{(ka-kb)^2}\left(e^{-\frac{1}{2}\left(ka+kb+\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)t}\left(-1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}\right)ka\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)$$

$$-\frac{1}{2\,(ka-kb)^2}\left(e^{-\frac{1}{2}\left(ka+kb+\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)t}\left(\left(1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(ka+kb+\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)t}\right)ka^2+ka\left(-2\left(1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(ka+kb+\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)t}\right)kb+\left(-1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)+kb\left(\left(1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}-2\,e^{\frac{1}{2}\left(ka+kb+\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)t}\right)kb+\left(-1+e^{\sqrt{-4\,ka\,kb+(ka+kb)^2}\,t}\right)\sqrt{-4\,ka\,kb+(ka+kb)^2}\right)\right)\right)$$

```
ttz = FullSimplify[zz[t] /. Sqrt[(ka - kb)^2] → ka - kb]
```

$$1-\frac{1}{2}\,e^{-\frac{1}{2}\left(ka+\sqrt{(ka-kb)^2}+kb\right)t}\left(1+e^{\sqrt{(ka-kb)^2}\,t}\right)-\frac{e^{-\frac{1}{2}\left(ka+\sqrt{(ka-kb)^2}+kb\right)t}\left(-1+e^{\sqrt{(ka-kb)^2}\,t}\right)(ka+kb)}{2\sqrt{(ka-kb)^2}}$$

```
ttz[[2, 2]]
```

$$e^{-\frac{1}{2}\left(ka+\sqrt{(ka-kb)^2}+kb\right)t}$$

```
ttx = FullSimplify[xx[t] /. Sqrt[(ka - kb)^2] → ka - kb]
```

$$\frac{1}{2\,(ka-kb)}\left(e^{-\frac{1}{2}\left(ka+\sqrt{(ka-kb)^2}+kb\right)t}\left(ka+e^{\sqrt{(ka-kb)^2}\,t}\,(ka-kb)-\left(-1+e^{\sqrt{(ka-kb)^2}\,t}\right)\sqrt{(ka-kb)^2}-kb\right)\right)$$

```
tty = FullSimplify[yy[t] /. Sqrt[(ka - kb)^2] → ka - kb]
```

$$\frac{e^{-\frac{1}{2}\left(ka+\sqrt{(ka-kb)^2}+kb\right)t}\left(-1+e^{\sqrt{(ka-kb)^2}\,t}\right)ka}{\sqrt{(ka-kb)^2}}$$

```
tty
```

$$\frac{e^{-\frac{1}{2}\left(ka+\sqrt{(ka-kb)^2}+kb\right)t}\left(-1+e^{\sqrt{(ka-kb)^2}\,t}\right)ka}{\sqrt{(ka-kb)^2}}$$

```
tty = Simplify[PowerExpand[tty]]
```

$$\frac{\left(e^{-ka\,t}-e^{-kb\,t}\right)ka}{-ka+kb}$$

These equations are identical to those derived in the text.