On the additivity of generation–recombination spectra. Part 1: Conduction band with two centres

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Abstract

If a semiconductor contains two generation–recombination centres, A and B, the noise spectrum either is the simple addition of the two characteristic A and B spectra, or a Lorentzian spectrum with a relaxation time \( \tau \) given by \( \tau^{-1} = \frac{1}{\tau_A} + \frac{1}{\tau_B} \). The latter situation is called mixing. We can derive the mathematical criterion that decides whether addition or mixing occurs: Addition if \( n_A > n_B \); \( n_A > n_B \). Mixing if \( n_A < n_B \). The number \( n \) is the number of free electrons in the conduction band. The number \( a \) either is \( a \), the number of occupied \( A \) states, or the number of empty states, \( (A-a) \), depending on which is smaller. A qualitative physical interpretation is given of the precise mathematical condition. © 2002 Elsevier Science B.V. All rights reserved.

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1. Stating the problem

The noise in the number of free electrons is clearly understood in the case of \( g-r \) processes between a conduction band and centres, all of the same type. Let us call the centres \( A \) centres. The noise spectrum is a Lorentzian:

\[
S_n(f) = \frac{4\tau_A}{(\Delta n)^2 + (2\pi f \tau_A)^2},
\]

where \( \tau_A \) is the lifetime of a fluctuation \( \Delta n \) in the number of free electrons. We shall call this spectrum (1) a characteristic \( A \) spectrum.

A complicated problem arises if we also have \( B \) centres in the sample. In some cases a simple addition of the characteristic \( A \) and the characteristic \( B \) spectrum is observed; in other cases only one Lorentzian is found with a characteristic time \( \tau \) given by

\[
\frac{1}{\tau} = \frac{1}{\tau_A} + \frac{1}{\tau_B}.
\]

Fig. 1 shows the two cases that we will call addition and mixing.

Our problem is under which conditions do we get mixing? When do we get addition? There has been a long tradition of studying the problem of two \( g-r \) centres. Recently, a survey was given by Van Vliet [1], which also mentions her own
fundamental paper [2] on the mathematical formalism needed for the discussion of our problem. But the complicated expressions obtained, do not give simple answers in terms of experimentally available data, concentrations, trap depths, temperature, etc. A straight answer to the question “When addition? When mixing?” was given by Hooge and Ren [3]. This answer was repeated in a review on $1/f$ noise sources [4]. The answer agrees with condition (25) of the present paper. Our paper differs from [3] in the way we manipulate the complicated equations and introduce convenient variables. This treatment makes the extension to more than two centres easy (to be discussed in another paper). We will make sure that the often rigorous approximations we used are indeed allowed. Part of the problem, mixing or addition, was discussed by van Rheenen, Bosman and van Vliet in a paper on “separate Lorentzians” [5]. In how far their conclusions agree with ours was already discussed in Ref. [3].

The extensive literature shows that many people studied the problem of two centres for its own sake. For the author of this paper, however, the inspiration came from a different angle. It is often assumed that $1/f$ noise is an addition of many g–r spectra. If the $\tau$-values are distributed according to

$$g(\tau)\,d\tau \propto \frac{1}{\tau} \,d\tau,$$

(3)

a $1/f$ spectrum results from the g–r spectra (1)

$$\int_0^\infty \frac{4\tau}{\tau + (2\pi f \tau)^2} \,d\tau = 4 \int_0^\infty \frac{1}{1 + x^2} \,dx \frac{1}{2\pi f} \,d\tau = \frac{4\pi}{2} \frac{1}{2\pi f} = \frac{1}{f}. \quad (4)$$

We are interested in the critical, but tacit assumption that the g–r spectra add, and that they do not mix. In the case of mixing, no $1/f$ spectrum will result from Eq. (3), but a single Lorentzian will appear with $\tau_L$ close to the smallest $\tau$

$$\frac{1}{\tau_L} = \sum_i \frac{1}{\tau_i} = \int_{\tau_1}^\infty \frac{1}{\tau} \,d\tau = \frac{1}{\tau_1} - \frac{1}{\tau_2} \approx \frac{1}{\tau_1}. \quad (5)$$

2. The characteristic $A$ spectrum

All quantities are defined in the left-hand part of Fig. 2

$$\Delta n = -\Delta a. \quad (6)$$

Fermi statistics:

$$\frac{d\Delta n}{dt} = \Delta G - \Delta R$$

$$= \gamma a(-\Delta n) + \gamma (N - n)\Delta a - \rho(A - a)\Delta n - \rho n(-\Delta a), \quad (7)$$

$$\frac{d\Delta n}{dt} = -G \left[\frac{1}{n} + \frac{1}{N - n} + \frac{1}{a} + \frac{1}{A - a}\right] \Delta n$$

$$= -\frac{1}{\tau_A} \Delta n. \quad (8)$$
In most cases the variance is the smallest number and $D$.

We will show later (53) that direct transitions between the centres and the band. In this model there are no spectrum. Fig. 2 shows the transitions between the introduced in Section 2 for the characteristic A.

For a simple A spectrum there is a single value of $\tau_A$ which is the lifetime of the fluctuations $\Delta n$ and $\Delta a$.

We introduce the following definitions

$$\frac{1}{n} = \frac{1}{n} + \frac{1}{N - n} \approx \frac{1}{n},$$

$$\frac{1}{a} = \frac{1}{a} + \frac{1}{A - a},$$

$$\frac{1}{m_A} = \frac{1}{n} + \frac{1}{a}. \quad (9)$$

Boltzmann statistics would give $n^* = n, a^* = a$.

From Eqs. (8) and (9) it follows that

$$\frac{1}{G\tau_A} = \frac{1}{m} = \frac{1}{n} + \frac{1}{a}. \quad (10)$$

We will show later (53) that $G\tau$ equals the variance

$$\langle \Delta n \rangle^2 = \langle \Delta a \rangle^2 = m. \quad (11)$$

In most cases the variance is the smallest number of $n, a$ and $(A - a)$. The spectral power density is given by the Lorentzian

$$S_n = \frac{4\langle \Delta n \rangle^2 \tau_A}{1 + (2\pi f \tau_A)^2} = \frac{4G^2}{1 + (2\pi f \tau_A)^2}. \quad (12)$$

3. One band, two centres A and B

The symbols and the notation is the same as introduced in Section 2 for the characteristic A spectrum. Fig. 2 shows the transitions between the centres and the band. In this model there are no direct transitions between the A and B centres. We do not assume anything about $(n + a + b)$, apart from $(n + a + b)$ being constant. A and B could be donors or acceptors. There could be additional deep acceptors that have captured a constant number of electrons. Therefore, we have relation (13) for the fluctuations

$$\Delta n = -\Delta a - \Delta b. \quad (13)$$

Calculation of $\tau_1$ and $\tau_2$

$$\frac{d\Delta a}{dt} = -\Delta G_A + \Delta R_A, \quad (14)$$

$$\frac{d\Delta n}{dt} = +\Delta G_A - \Delta R_A + \Delta G_B - \Delta R_B, \quad (15)$$

$$\frac{d\Delta b}{dt} = -\Delta G_B + \Delta R_B. \quad (16)$$

For each centre we use equations analogous to Eq. (7). The signs follow from the definition of the symbols $G$ and $R$ for generation and recombination processes of free electrons, which gives opposite signs for trapped electrons. Because of Eq. (13) we have only two independent equations: Eq. (14) for $\Delta a$ and Eq. (16) for $\Delta b$. By using Eq. (13) we eliminate the $\Delta n$ terms from $\Delta G_A$ etc.

We define a relaxation time $\tau$ and its inverse $\vartheta$

$$\frac{d\Delta x}{dt} = -\frac{1}{\tau} \Delta x = -\vartheta \Delta x. \quad (17)$$

Relations (14) and (16) then become

$$\vartheta \Delta a = G_A \left( \frac{1}{a} + \frac{1}{n} \right) \Delta a + G_A \left( \frac{1}{n} \right) \Delta b$$

$$= \vartheta \Delta a + \frac{G_A}{n} \Delta b, \quad (18)$$

$$\vartheta \Delta b = G_B \left( \frac{1}{n} \right) \Delta a + G_B \left( \frac{1}{b} + \frac{1}{n} \right) \Delta b$$

$$= \frac{G_B}{n} \Delta a + \vartheta \Delta b. \quad (19)$$

The symbols $A$ and $B$ are chosen in such a way that by definition

$$\vartheta_A > \vartheta_B \quad (20)$$

Eqs. (18) and (19) can be rewritten as

$$\left( \vartheta_A - \vartheta \right) \Delta a + \frac{G_A}{n} \Delta b = 0, \quad (21)$$

$$\frac{G_B}{n} \Delta a + \left( \vartheta_B - \vartheta \right) \Delta b = 0. \quad (22)$$
Excluding the trivial solutions $\Delta a = 0, \Delta b = 0$, two values for $\vartheta$ follow from

$$
\begin{bmatrix}
\vartheta_A - \vartheta \\
\frac{G_A}{n} \\
\vartheta_B - \vartheta
\end{bmatrix} = 0.
$$

(23)

So $\Delta a$ will decay as a linear combination of two exponentials

$$
\Delta a(t) = \Delta a_1(t) + \Delta a_2(t)
$$

$$
= \Delta a_1(0)e^{-\vartheta_1 t} + \Delta a_2(0)e^{-\vartheta_2 t}.
$$

(24)

Up till here no approximations are used. For an easy manipulation of the complicated expressions we now introduce approximations in two steps:

1. **Rigorous approximation**: This gives a neatly arranged, systematic overview with surprisingly accurate results.

2. **Less rigorous approximations**: This demonstrates that, in general, the rigorous approximation is correct. With this we find finite small values for $\vartheta$, if the rigorous approximation gives $\vartheta = 0$.

### 3.1. Rigorous approximation

In expression (10) for $\vartheta_A$ and $\vartheta_B$ we completely neglect the smaller terms. If $n \ll a^*, n \ll b^*$ we have $\vartheta_A = G_A/\vartheta$, $\vartheta_B = G_B/\vartheta$. The off-diagonal elements in Eq. (23) equal $\vartheta_B$; if $n \gg a^*, n \gg b^*$ we have $\vartheta_A = G_A/a^*, \vartheta_B = G_B/b^*$. The off-diagonal elements in Eq. (23) become zero.

The exact Eq. (23) can now be rewritten in the rigorous approximation for the two situation as:

$$
\begin{bmatrix}
\vartheta_A - \vartheta \\
\frac{G_A}{n} \\
\vartheta_B - \vartheta
\end{bmatrix} = 0.
$$

(25)

### 3.2. Less rigorous approximation

**Mixing $n \ll a^*, b^*$.** The off-diagonal elements in Eq. (23) do not precisely equal $\vartheta_A$ and $\vartheta_B$. Eq. (23) then gives a quadratic expression in $\vartheta$ with the approximate solutions.

$$
\vartheta_1 = \vartheta_A + \vartheta_B - \frac{n}{b^*}\vartheta_B \approx \vartheta_A + \vartheta_B.
$$

$$
\vartheta_2 = 0 + \frac{n}{b^*}\vartheta_B = \frac{G_B}{b^*}.
$$

(26)

Later in Eq. (33) we will need an even more accurate expression for $\vartheta_2$, when we calculate very small values of $\Delta n$. Using Eq. (10) we therefore write, the exact expression (23) as

$$
\begin{vmatrix}
1 + \frac{n}{a^*} - \frac{\vartheta_2}{\vartheta_A} & 1 \\
1 & 1 + \frac{n}{b^*} - \frac{\vartheta_2}{\vartheta_B}
\end{vmatrix}.
$$

(27)

As we already know that $\vartheta_2 \ll \vartheta_A, \vartheta_B$, (27) leads to the approximation

$$
\vartheta_2 = \frac{n\left(\frac{1}{a^*} + \frac{1}{b^*}\right)}{\vartheta_A + \vartheta_B}
$$

$$
= \frac{n}{c} \frac{\vartheta_A \vartheta_B}{\vartheta_A + \vartheta_B} \text{ with } \frac{1}{c} = \frac{1}{a^*} + \frac{1}{b^*}.
$$

(28)

With the approximations $b^* \ll a^*$, and $\vartheta_B \ll \vartheta_A$ this again leads to $\vartheta_2 = (n/b^*)\vartheta_B$ in agreement with Eq. (26).

**Fig. 3** suggests that if we take $\vartheta_B \ll \vartheta_A$, we will have $b^* < a^*$. In the following we restrict ourselves to this very probable situation, and use approximation (26). Strictly speaking, however, it is possible that $b^* > a^*$ if $\vartheta_B \ll \vartheta_A$. The result for the problem “addition or mixing” is essentially the same.

### 3.3. Addition, $n \gg a^*, b^*$

Starting from Eq. (23) we obtain a quadratic expressing in $\vartheta$ from which we find

$$
\vartheta_1 = \vartheta_A + \frac{n}{G_A} \frac{\vartheta_B}{\vartheta_A - \vartheta_B} \approx \vartheta_A + \frac{a^* b^*}{n} \frac{\vartheta_B}{\vartheta_A - \vartheta_B} \approx \vartheta_A,
$$

$$
\vartheta_2 = \frac{n}{G_B} \frac{\vartheta_A}{\vartheta_B} \frac{\vartheta_B}{\vartheta_A - \vartheta_B} \approx \frac{a^* b^*}{n} \frac{\vartheta_A}{\vartheta_B} \approx \vartheta_B.
$$
4. Magnitudes and correlations

4.1. Mixing

The fluctuations $\Delta a$ and $\Delta b$ are calculated from the determinant (23), which summarizes the Eqs. (21) and (22).

Rigorous approximation:

$$\vartheta_1 = \vartheta_A + \vartheta_B \rightarrow \Delta b_1 = \frac{\vartheta_B}{\vartheta_A} \Delta a_1,$$

$$\Delta n_1 = - \left(1 + \frac{\vartheta_B}{\vartheta_A}\right) \approx - \Delta a_1,$$

$$\vartheta_2 = 0 \rightarrow \Delta b_2 = - \left(1 + \frac{n}{a^2}\right) \Delta a_2,$$

$$\Delta n_2 = \frac{n}{a^2} \Delta a_2.$$

The result (33) follows from the exact relation (23), if we divide the upper row by $G_A/n$ and the lower row by $G_B/n$:

$$\left| 1 + \frac{n}{a^2} - n \left(1 + \frac{1}{b^2}\right) \frac{\vartheta_A}{\vartheta_B} \right| \approx 1 + \frac{n}{b^2} - n \left(1 + \frac{1}{b^2}\right) \Rightarrow 1 - \frac{n}{a^2} \approx 0. \quad (34)$$

We will now discuss the correlations between the fluctuation components. Therefore, we consider the fluctuations due to the shot noise in $G_A$ and $R_A$ which refer to as “from $A$”. In a very short time interval $\delta t$, the two processes transport $a_\delta$ electrons from the $A$ centres into the band:

$$a_\delta = G a_\delta - R a_\delta = G \bar{a}_\delta - R \bar{a}_\delta + G \Delta a_\delta - R \Delta a_\delta$$

$$= 0 + \Delta a_\delta. \quad (35)$$

If $\delta t \ll \tau_A, \tau_B, \tau_1, \tau_2$, the fluctuation $\Delta a_\delta$, built up at the end of the interval $\delta t$, has not suffered from any direct or indirect recombination. At the end of the interval, which we denote by $t = 0$, the recombination with $\vartheta_1$ and $\vartheta_2$ set in, so that the fluctuations $\Delta a_\delta$ decay according to

$$\Delta a_\delta(t) = \Delta a_{\delta 1}(0) e^{-\vartheta_{\delta 1} t} + \Delta a_{\delta 2}(0) e^{-\vartheta_{\delta 2} t}. \quad (36)$$

At $t = 0$ from $A$:

$$A \Delta a_\delta = A \Delta a_{\delta 1} + A \Delta a_{\delta 2},$$

$$A \Delta b_{\delta 1} + A \Delta b_{\delta 2} = 0. \quad (37)$$

At $t = 0$ from $B$

$$B \Delta a_\delta = B \Delta a_{\delta 1} + B \Delta a_{\delta 2},$$

$$B \Delta a_{\delta 1} + B \Delta a_{\delta 2} = 0. \quad (38)$$

$$\langle A \Delta a_\delta \cdot B \Delta b_\delta \rangle = 0. \quad (39)$$

The free electrons in the conduction band cannot be distinguished as electrons from $A$ and electrons from $B$. Therefore, we do not attach the subscripts
$A$ or $B$ to $n$, but attach them to the $\Delta$ symbols. From now on we drop $(t = 0)$ or $(0)$ in $A\Delta a(0)$ to simplify the relations.

The fluctuation $A\Delta a_\delta$ is the value of $A\Delta a$ generated in the interval $0 < t < \delta t$. Its relation to the variance $(\Delta a)^2$ will be discussed later in Eq. (54).

We have 4 unknowns, $A\Delta a_{\delta 1}$, $A\Delta a_{\delta 2}$, $A\Delta b_{\delta 1}$, $A\Delta b_{\delta 2}$, and 4 Eqs. (21) and (22) and two in Eq. (37) from $A$. And we have 4 unknowns and 4 Eqs. (21) and (22) and two in Eq. (38) from $B$. The solutions are as follows:

From $A$:

$A\Delta a_{\delta 1} = \left(1 - \frac{\partial B}{\partial A}\right)\Delta a_\delta \approx \Delta a_\delta$,

$A\Delta a_{\delta 2} = \frac{\partial B}{\partial A}\Delta a_\delta \approx 0$,

$A\Delta b_{\delta 1} = \frac{\partial B}{\partial A}\Delta a_\delta \approx 0$,

$A\Delta b_{\delta 2} = -\frac{\partial B}{\partial A}\Delta a_\delta \approx 0$,

$A\Delta n_{\delta 1} = -\Delta a_\delta$,

$A\Delta n_{\delta 2} = \frac{n}{a^2 A}\Delta a_{\delta 2} = \frac{n}{a^2 A}\frac{\partial B}{\partial A}\Delta a_\delta \approx 0$ from (33). (40)

From $B$:

$B\Delta a_{\delta 1} = \left(1 - \frac{\partial B}{\partial A}\right)\Delta b_\delta \approx \Delta b_\delta$,

$B\Delta a_{\delta 2} = -\left(1 - \frac{\partial B}{\partial A}\right)\Delta b_\delta \approx -\Delta b_\delta$,

$B\Delta b_{\delta 1} = \frac{\partial B}{\partial A}\Delta b_\delta \approx 0$,

$B\Delta b_{\delta 2} = \left(1 - \frac{\partial B}{\partial A}\right)\Delta b_\delta \approx \Delta b_\delta$,

$B\Delta n_{\delta 1} = -\Delta b_\delta$,

$B\Delta n_{\delta 2} = \frac{n}{a^2 B}\Delta a_{\delta 2} = \frac{n}{a^2 A}\Delta b_\delta \approx 0$ from (33). (41)

From the relations (40) and (41) it follows that the spectrum of $n$ does not have a $\partial_2$ component in the rigorous approximation. These results are summarized in Fig. 4.

4.2. Addition

The calculation of the 8 unknowns, $A\Delta a_{\delta 1}...A\Delta b_{\delta 2}$, follows the same procedure as in the case of mixing. The rigorous approximation gives a very simple result:

$A\Delta a_{\delta 1} = \Delta a_\delta$  $B\Delta b_{\delta 1} = \Delta b_\delta$. (42)

All other components are zero.

Since it is doubtful whether it is correct to neglect the off-diagonal elements completely, we shall now work out the less rigorous
approximation. We rewrite the exact determinant (23) as (43).

\[
\begin{vmatrix}
\theta_A - \theta & \frac{a^*}{n}\theta_A \\
\frac{b^*}{n}\theta_B & \theta_B - \theta
\end{vmatrix} = 0.
\] (43)

Using \(\theta_1\) and \(\theta_2\) from (37) we obtain

\[
\theta_1 : \begin{vmatrix}
\frac{b^*}{n}\theta_B & \theta_A \\
\frac{b^*}{n}\theta_B & \theta_A
\end{vmatrix} = 0 \quad \text{and} \quad \theta_2 : \begin{vmatrix}
1 & \frac{a^*}{n} \\
1 & \frac{a^*}{n}
\end{vmatrix} = 0.
\] (44)

From the Eqs. (37) and (38), analogous to Eqs. (40) and (41), we find, from A:

\[
A\Delta a_{\delta 1} = \Delta a_{\delta} \approx \Delta a_{\delta} \\
A\Delta a_{\delta 2} = \frac{a^*}{n} \frac{b^*}{n} \theta_B \Delta a_{\delta} \approx 0, \\
A\Delta b_{\delta 1} = \frac{b^*}{n} \theta_B \Delta a_{\delta} \approx 0, \\
A\Delta b_{\delta 2} = -\frac{b^*}{n} \theta_B \Delta a_{\delta} \approx 0, \\
A\Delta n_{\delta 1} = -\left(1 + \frac{b^*}{n} \theta_B\right) \Delta a_{\delta} \approx -\Delta a_{\delta}, \\
A\Delta n_{\delta 2} = \frac{b^*}{n} \theta_B \Delta a_{\delta} \approx 0.
\] (45)

From B:

\[
B\Delta a_{\delta 1} = \frac{a^*}{n} \Delta b_{\delta} \approx 0, \\
B\Delta b_{\delta 2} = \frac{a^*}{n} \Delta b_{\delta} \approx 0, \\
B\Delta b_{\delta 1} = \frac{a^*}{n} \frac{b^*}{n} \theta_B \Delta b_{\delta} \approx 0, \\
B\Delta n_{\delta 1} = -\left(1 - \frac{a^*}{n} \frac{b^*}{n} \theta_B\right) \Delta b_{\delta} \approx -\Delta b_{\delta}, \\
B\Delta n_{\delta 2} = -\left(1 - \frac{a^*}{n}\right) \Delta b_{\delta} \approx 0.
\] (46)

These results are summarized in Fig. 5.

5. Variances and spectra

For the calculation of a noise spectrum we need the variance. The variances of \(\Delta a, \Delta b,\) and \(\Delta n\) are known. In a previous publication [6] we derived them from statistical mechanics. Therefore, the expressions found there do not contain any parameter related to kinetics like \(\tau_a\) or \(\tau_b:\)

\[
\frac{1}{\langle\Delta a^2\rangle} = \frac{1}{a^* + b^* + n}, \\
\frac{1}{\langle\Delta b^2\rangle} = \frac{1}{b^* + a^* + n}, \\
\frac{1}{\langle\Delta n^2\rangle} = \frac{1}{n + a^* + b^*}.
\] (47)

---

Fig. 5. Left: Relations between the fluctuation components and \(\Delta a_{\delta}\). Right: The same for \(\Delta b_{\delta}\). The fluctuations \(\Delta a_{\delta}\) and \(\Delta b_{\delta}\) are uncorrelated.
5.1. Conduction band with one centre

We first treat a conduction band with $A$ centres only. The result is trivial, but the treatment demonstrates the formalism, which later will be extended to the not at all trivial case with $A$ and $B$ centres. We follow the same line of reasoning as with the relations (35)–(39). In a very short time interval $\delta t(\delta t \ll \tau_A)$, the average number of electrons transported from $A$ to the band is $\overline{n_A}$. Since the generation process is a Poissonian

$$\overline{(\Delta n_A)^2} = \overline{n_A} = \bar{G} \delta t. \quad (50)$$

The same applies to the recombination process $R$.

$$\overline{(\Delta n_B)^2} = \overline{n_B} = \bar{G} \delta t. \quad (51)$$

The fluctuation $\Delta n_B$ then starts to decay exponentially with a lifetime $\tau_A$. Its contribution to the variance is

$$\overline{(\Delta n_B)^2} = \frac{1}{T} \int_0^T [\Delta n_B e^{-t/\tau_A}]^2 dt = \frac{1}{T} 2 \bar{G} \delta t \int_0^T [e^{-t/\tau_A}]^2 dt. \quad (52)$$

There are $T/\delta t$ contributions from such intervals $\delta t$.

With $\delta t \ll \tau_A < T_A$ the variance becomes

$$\overline{(\Delta n)^2} = \frac{T}{\delta t} \int_0^T \left[ e^{-t/\tau_A} \right]^2 dt = 2 \bar{G} \delta t = \bar{G} \tau_A, \quad (53)$$

in agreement with Eq. (10).

The square brackets in Eqs. (52) and (53) are superfluous, but they indicate where we will substitute more complicated expressions in the case of two centres.

Summarizing, the relation between $\langle (\Delta n_A)^2 \rangle$ and the variance $\langle (\Delta n)^2 \rangle$ is as follows:

$$\overline{(\Delta n_A)^2} = 2 \bar{G} \delta t = \bar{G} \tau_A \frac{2 \delta t}{\tau} = \overline{(\Delta n)^2} \frac{2 \delta t}{\tau}. \quad (54)$$

5.2. Mixing

We now consider $\Delta a_A, \Delta b_A$, and $\Delta n_B$. The relations (36)–(41) and Fig. 4 show that $\Delta a_A$ does not decay as a single exponent, but as a sum of two components with $\tau_1$ and $\tau_2$. We find the variance by integration of the exponential decay functions of $\langle \Delta a_A \rangle^2$ in the same way as with the Eqs. (52) and (53).

To keep the notation simple and use fast approximations, we write

$$e \equiv \frac{\delta B}{\delta B} = \frac{\tau_A}{\tau_B} \ll 1,$$

$$\bar{g}_1 = \bar{g}_A + \bar{g}_B = \bar{g}_A(1 + e),$$

$$\bar{g}_2 = \frac{1}{\bar{a}} + \frac{1}{\bar{b}} \approx \frac{n}{c} \approx (1 - e) \bar{g}_B,$$

$$\bar{g}_A - \bar{g}_B \approx \frac{1}{\bar{a}} + \frac{1}{\bar{b}}$$

with $\frac{1}{c} \equiv \frac{1}{\bar{a}} + \frac{1}{\bar{b}}$ from (25).

We first derive the variance of $a$. Using Eqs. (40), (41) and (54) we find for $\Delta a = \Delta a_1 + \Delta a_2$ “from $A$”

$$\overline{(\Delta a)^2} = \frac{T}{\delta t} \int_0^T \langle \Delta a \rangle^2 dt \times \left( \int_0^T [(1 - e) e^{-t/\tau_1} + e e^{-t/\tau_2}]^2 dt, \right.$$

$$2 \bar{G}_A \int_0^T [(1 - e)^2 e^{-2\delta t} + 2(1 - e) e^{-(\delta t + \eta)} + e^2 e^{-2\delta t}] dt \approx m_A \left(1 + \frac{c}{n} \right). \quad (56)$$
In a similar way

\[ (\Delta a)^2 \approx m_B (1 - \varepsilon) \frac{c}{n}, \] (57)

The variance follows from Eqs. (56) and (57); taking into account \( n \ll a^*, b^* \) and \( m_a \approx m_b \approx n \)

\[ (\Delta a)^2 = (\Delta a_1)^2 + (\Delta a_2)^2, \]

\[ = m_A \left( 1 + \varepsilon \frac{c}{n} \right) + m_B (1 - \varepsilon) \frac{c}{n} \]

\[ = n + c \approx c = \frac{a^* b^*}{a^* + b^*} \]

in agreement with Eq. (47).

The variance of \( b \) is derived in the same way

\[ (\Delta b)^2 \approx m_B \frac{c}{n}, \] (59)

\[ (\Delta b)^2 \approx m_B (1 - \varepsilon) \frac{c}{n}, \] (60)

For the variance of \( b \) we find

\[ (\Delta b)^2 = (\Delta b_1)^2 + (\Delta b_2)^2, \]

\[ = m_A \frac{c}{n} + m_B (1 - \varepsilon) \frac{c}{n} \approx c = \frac{a^* b^*}{a^* + b^*} \] (61)

in agreement with Eq. (47) as \( n \ll a^*, b^*. \)

As required by theory, the approximations for \( \langle \Delta a^2 \rangle \) and \( \langle \Delta b^2 \rangle \) do not contain parameters related to kinetics, such as \( \tau_A, \tau_B, \) or \( \varepsilon. \) Only equilibrium concentrations are involved, expressed as \( a^*, b^* \) or \( c. \)

5.3. Variance and spectrum of \( \Delta n \)

We first calculate four components that contribute to \( \langle \langle \Delta n \rangle^2 \rangle. \) We use (40), (41) and approximations (55)

From \( A: \)

\[ (\Delta n_1)^2 = G_A \tau_1 \approx G_A \tau_A = m_A = n, \] (62)

\[ (\Delta n_2)^2 = G_A (\frac{n}{a^*}) \tau_2 \approx G_A \tau_A = m_A = a^*, \]

\[ \approx G_A \tau_A (\frac{n}{a^*}) \approx G_A \tau_A = m_A = a^*. \]

\[ \approx G_A \tau_A (\frac{n}{a^*}) \approx G_A \tau_A = m_A = a^*. \]

From \( B: \)

\[ (\Delta n_1)^2 = G_B \tau_1 \approx G_B \tau_B = m_B = \varepsilon n, \]

\[ \approx G_B \tau_B = m_B = b^*. \]

\[ \langle \Delta n \rangle^2 \approx (\Delta n_1)^2 + (\Delta n_2)^2, \]

\[ \approx G_B \tau_B = m_B = b^*. \]

\[ (\Delta n_2)^2 = G_B \left( \frac{n}{a^*} \right) \tau_2 \approx G_B \tau_B = m_B = a^*, \]

\[ \approx G_B \tau_B = m_B = b^*. \]

For \( S_1, \) the Lorentzian with \( \tau_1, \) we need \( \langle \langle \Delta n_1 \rangle^2 \rangle. \)

Since \( \Delta n_1 \) and \( \Delta n_2 \) are uncorrelated

\[ (\Delta n_2)^2 = (\Delta n_1)^2 + (\Delta n_2)^2 = n + \varepsilon n \approx n. \] (63)

The spectrum becomes

\[ S_1 = \frac{4n \tau_1}{1 + (2\pi f \tau_1)^2}. \] (64)

For \( S_2, \) the Lorentzian with \( \tau_1, \) we use \( \langle \langle \Delta n_2 \rangle^2 \rangle. \)

Here, too, we have two uncorrelated terms

\[ (\Delta n_2)^2 = (\Delta n_1)^2 + (\Delta n_2)^2 = \varepsilon \left( \frac{n}{a^*} \right)^2 \approx \left( \frac{n}{a^*} \right)^2 \]

\[ S_2 = \frac{4(n/a^*)^2 \varepsilon}{1 + (2\pi f \tau_2)^2}. \] (66)

At very low frequencies the spectrum \( S_2 \) can be observed if its white branch, \( 4(n/a^*)^2 \varepsilon, \) is above the white branch of \( S_1, 4n \tau_1. \) The condition for a visible \( S_2 \) is

\[ \left( \frac{b^*}{a^* + b^*} \right)^2 > \varepsilon, \] (67)

which is possible but not necessary.

5.4. Addition

In the case of addition \( (n \gg a^*, b^*), \) the calculations of the variances and spectra are very simple. We use the results (45) and (46) in the rigorous approximation and the approximations \( \tau_1 = \tau_A, \tau_2 = \tau_B \)

\[ \langle \langle \Delta n_1 \rangle^2 \rangle = \langle \langle \Delta n_2 \rangle^2 \rangle = \langle \langle \Delta n_3 \rangle^2 \rangle = \langle \langle \Delta n_4 \rangle^2 \rangle, \]

\[ \approx G_A \tau_A = m_A = a^*, \]

\[ \approx G_B \tau_B = m_B = b^*, \]

\[ \approx G_B \tau_B = m_B = b^*, \]

\[ \approx G_B \tau_B = m_B = b^*. \]

\[ \approx G_B \tau_B = m_B = b^*. \]

\[ (\Delta a)^2 = G_A \tau_1 = a^*, \]

\[ (\Delta b)^2 = G_B \tau_2 = b^*, \] (72)
Eqs. (70)–(71) are in agreement with Eq. (47) as \( n \gg a^*, b^* \).

For the spectra we find

\[
S_1 = \frac{4a^* \tau_A}{1 + (2\pi f \tau_A)^2}, \tag{73}
\]

\[
S_2 = \frac{4b^* \tau_B}{1 + (2\pi f \tau_B)^2}. \tag{74}
\]

The resulting spectrum simply is the addition of the two characteristic \( A \) and \( B \) Lorentzians.

6. Discussion for the results

We will now discuss four principle results from the previous sections.

Result 1: Whether mixing or addition occurs is determined by the magnitude of \( n \) compared to \( a^* \) and \( b^* \).

Result 2: If \( n \ll a*, b* \) we have mixing with \( \beta_1 = \beta_A + \beta_B \) and \( \beta_2 \to 0 \).

Result 3: If \( n \gg a*, b* \) we have addition with \( \beta_1 = \beta_A \) and \( \beta_2 = \beta_B \).

Result 4: The spectra are given by the relations (64) and (66), and by (73) and (74).

The calculations showed that the problem “mixing or addition” is not a simple one. The solution follows from complicated calculations. Even for our approximated results, 74 equations were required. When we now try to describe the kinetics, we can only give a qualitative picture. We do not aim at accuracy, completeness or formal rigour. We look for properties that are essential for the differences between a system that gives mixing and one that gives addition. The discussion is based on Eqs. (13)–(16). We write Eq. (15) as

\[
\frac{d\Delta n}{dt} = G_A \frac{\Delta a}{a} - R_A \left( \frac{\Delta n}{n} + \frac{\Delta a}{A-a} \right) - R_B \left( \frac{\Delta n}{n} + \frac{\Delta b}{B-b} \right) + G_B \frac{\Delta b}{b}. \tag{75}
\]

Rearranging the terms leads to

\[
- \frac{d\Delta a}{dt} - \frac{d\Delta b}{dt} = \frac{d\Delta n}{dt} = \left[ \frac{R_A}{a^*} + \frac{R_A}{n} + \frac{R_B}{n} \right] \Delta a
+ \left[ \frac{R_A}{n} + \frac{R_B}{n} + \frac{R_B}{b^*} \right] \Delta b \tag{76}
\]

In Eq. (75) it is clear to which transition a term corresponds. However, Eq. (76) is obtained from Eq. (75) by using relations like \( G_A = R_A \) and \( -\Delta n = \Delta a + \Delta b \). For example, we substitute \( R_A \) for \( G_A \) because they have the same numerical value. The term \( R_A/a^* \) in Eq. (76) does not mean that we only consider the recombination of electrons from the band to \( A \); here \( G_A/a \) from Eq. (75) is included as well. Do the denominators \( a^*, b^* \) and \( n \) indicate where the transition starts? Not necessarily. The term \( R_A \Delta a/(A-a) \) in Eq. (75) is combined with \( G_A \Delta a/a \) in Eq. (75) to form \( R_A \Delta a/a^* \) in Eq. (76). This \( a^* \) term describes both electrons going from \( A \) to the band and free electrons \( n \) falling into the \( (A-a) \) empty levels. The well-chosen parameter \( a^* \) makes the calculations easy, but \( a^* \) makes it difficult to visualize simple schemes of transitions as given in Fig. 2. For classical particles or for Fermions with the Fermi level far below the centres, \( a^* \) simply is \( a \). Then a denominator in Eq. (76) still shows the transition under consideration, which makes the qualitative discussion easy. This does not mean that Boltzmann statistics or Boltzmann approximations are required for the results of our calculations. All calculations with \( a^* \) and \( b^* \) were based on Fermi statistics, but in the following qualitative discussion transitions of classical particles are considered. We then discuss a situation that occurs with electrons in a semiconductor with a Fermi level well below the centres.

In Eq. (76) the decay of \( \Delta a \) is determined by three terms: one transition from \( A \) and two from the band. The criterion \( n \ll a^*, b^* \) makes it possible to neglect some of the terms between square brackets. Such negligible terms are written with factors \( \{x/y\} \ll 1 \).

6.1. Addition \( n \gg a^*, b^* \)

Using \( \beta_A = R_A/a \) and \( \beta_B = R_B/b \) Eq. (76) becomes

\[
\frac{d\Delta a}{dt} - \frac{d\Delta b}{dt} = \left[ \beta_A + \left( \frac{a}{n} \right) \beta_A + \left( \frac{b}{n} \right) \beta_B \right] \Delta a
+ \left[ \left( \frac{a}{n} \right) \beta_A + \left( \frac{b}{n} \right) \beta_B + \beta_B \right] \Delta b
\approx \beta_A \Delta a + \beta_B \Delta b. \tag{77}
\]
Fluctuations $\Delta a$ and $\Delta b$ decay with $\bar{d}_A$ and $\bar{d}_B$, respectively. Thus the decay of $\Delta n$ is described by two exponentials, yielding two Lorentzians in $S_n$. For this case Fig. 6 shows two uncorrelated noise sources in the transitions from $A$ and $B$.

6.2. Mixing $n \ll a^*, b^*$

Using $\bar{d}_A = R_A/n$ and $\bar{d}_B = R_B/n$ Eq. (76) becomes

$$\frac{d\Delta a}{dt} - \frac{d\Delta b}{dt} = \frac{d\Delta n}{dt} = \left[\left\{\frac{n}{a}\right\}\bar{d}_A + \bar{d}_A + \bar{d}_B\right] \Delta a$$

$$+ \left[\bar{d}_A + \bar{d}_B + \left\{\frac{n}{b}\right\}\bar{d}_B\right] \Delta b$$

$$\approx (\bar{d}_A + \bar{d}_B) \Delta a + (\bar{d}_A + \bar{d}_B) \Delta b$$

$$= -(\bar{d}_A + \bar{d}_B) \Delta n.$$

(78)

The fluctuations $\Delta a$ and $\Delta b$, and thus $\Delta n$ too, decay all with the same $\bar{d}_1 = \bar{d}_A + \bar{d}_B$. For this case Fig. 6 shows that the important transitions are two correlated transitions from the same $\Delta n$, going to the $A$ and $B$ centres in a fixed ratio $\bar{d}_A : \bar{d}_B$. This continues till $\Delta n$ is practically zero (see Fig. 4). Then we arrive at the situation in which $\Delta a = -\Delta b$, which is rather stable, since all transport between $A$ and $B$ is by the very few electrons in the band. This explains the extremely long relaxation time $\tau_2$. An essential requirement for the relaxation time $\tau_2$ to be long is that there are no direct transitions between $A$ and $B$ centres.

We consider a situation in which $\beta$ electrons are removed from the $B$ level to the $A$.

$$\Delta n \ll \Delta a = \beta = -\Delta b.$$  

(79)

If $\bar{d}_B \gg \bar{d}_A$ the fast processes between $A$ and the band lead to a quasi equilibrium with $G_A \Delta a / a = R_A \Delta n / n$.

The "equilibrium" populations are as follows

$$\Delta n = \left\{\frac{n}{a}\right\} \Delta a = \left\{\frac{n}{a}\right\} \beta,$$

$$\Delta n = \left(1 - \left\{\frac{n}{a}\right\}\right) \beta \approx \beta,$$

(80)

$$\Delta b = -\beta.$$

Because of the low value of $\Delta n$, very few electrons, now in $A$, will return to $B$ via the band (Fig. 6).

$$\frac{d\Delta b}{dt} = \Delta n \bar{d}_B = \left\{\frac{n}{a}\right\} \beta \bar{d}_B = -\Delta b \left\{\frac{n}{a}\right\} \bar{d}_B.$$

(81)

The population in $B$ also changes because of the generation process to the band

$$\frac{d\Delta b}{dt} = -(-\beta) \left\{\frac{n}{a}\right\} \bar{d}_B = -\Delta b \left\{\frac{n}{a}\right\} \bar{d}_B.$$

(82)

These electrons immediately fall from the band into the $A$ level. The result of the two processes (81) and (82) at the $B$ level is

$$\bar{d}_2 = \left\{\frac{n}{a} + \frac{n}{b}\right\} \bar{d}_B$$

(83)

being in surprisingly good agreement with Eq. (28).

Characteristic for mixing is that recombination processes from the band dominate over generation processes from the centres. The fast recombination with $\bar{d}_1 = \bar{d}_A + \bar{d}_B$ results from decay of the same $\Delta n$ to the centres with a fixed ratio $\bar{d}_A : \bar{d}_B$. The final very slow decay follows from the low number $\Delta n \rightarrow 0$, making indirect transport between $A$ and $B$ very difficult.

In a following publication we will investigate whether it is possible to construct a $1/f$ spectrum from many generation–recombination spectra. Both situations, mixing and addition, look promising. Mixing gives spectra at frequencies well below the characteristic $A$- and $B$-frequencies.

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**Fig. 6.** Dominant transitions of the fluctuations.
Addition is the very essence of the widely used models of Surdin [7], McWhorter [8] and others.

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References