Flux-quantization by Bäcklund transformations in a model of electrodiffusion based on Painlevé II

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A simple problem in steady-state electrodiffusion:

(Nernst 1888, Planck 1890, Grafov & Chernenko 1962, Bass 1964)

$$\Phi_+ = -D_+ \, {c_+}'(x) + (zeD_+/kT) \, E(x) \, c_+(x)$$

$$\Phi_- = -D_- \, {c_-}'(x) - (zeD_-/kT) \, E(x) \, c_-(x)$$

$$E'(x) = (4\pi ze/\epsilon) \, [c_+(x) - c_-(x)]$$

for $0 < x < \delta$.

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$$E'(x) = (4\pi ze/\epsilon)\,[c_+(x) - c_-(x)]$$

for $0 < x < \delta$.

Current density: $J = ze\,(\Phi_+ - \Phi_-)$

In dimensionless form:

$$c_+{}'(x) = E(x)\, c_+(x) - \Phi_+$$

$$c_-{}'(x) = -E(x)\, c_-(x) - \Phi_-$$

$$\lambda^2 E'(x) = c_+(x) - c_-(x)$$

for $0 < x < 1$, and

$$J = \alpha_+ \Phi_+ - \alpha_- \Phi_-$$

Here $\alpha_\pm > 0$ are known constants, with $\alpha_+ + \alpha_- = 1$

and

$$\lambda = \frac{1}{\delta}\sqrt{\frac{\epsilon k T}{4\pi z^2 e^2\, c_{ref.}}} > 0$$

Planck took $\lambda \approx 0$, implying electroneutrality:

$$c_+(x) = c_-(x) = c(x) = c(0) + [c(1) - c(0)]x$$

$$E(x) = (\Phi_+ - \Phi_-)/2c(x)\,, \quad \Phi_+ + \Phi_- = 2[c(0) - c(1)]$$

$$J = \alpha_+\Phi_+ - \alpha_-\Phi_- \, (= J_0\,, \quad \text{say})$$

— only an approximate solution of the system of ODEs.

When $E(x) = 0$, Planck's approximate solution becomes exact:

$$c_+(x) = c_-(x) = c(x) = c(0) + [c(1) - c(0)]x$$

$$E(x) = 0\,, \quad \Phi_+ = \Phi_- = [c(0) - c(1)]$$

$$J = J_0 = (\alpha_+ - \alpha_-)[c(0) - c(1)]$$

A typical BV problem:

Given the BCs

$$c_+(0) = c_-(0) = c_0$$

$$c_+(1) = c_-(1) = c_1$$

$$J = J_0$$

find

$$c_+(x)\,, \quad c_-(x)\,, \quad E(x)\,, \quad \Phi_+\,, \quad \Phi_-$$

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Planck's exact solution is a (the?) solution when

$$J_0 = (\alpha_+ - \alpha_-)[c_0 - c_1]$$

A first-integral:

$$
\begin{aligned}
{c_+}'(x) + {c_-}'(x) &= E(x)[c_+(x) - c_-(x)] - (\Phi_+ + \Phi_-) \\
&= \lambda^2 E(x) E'(x) - (\Phi_+ + \Phi_-)
\end{aligned}
$$

A first-integral:

$$c_+{}'(x) + c_-{}'(x) = E(x)[c_+(x) - c_-(x)] - (\Phi_+ + \Phi_-)$$

$$= \lambda^2 E(x) E'(x) - (\Phi_+ + \Phi_-)$$

$$\Rightarrow \quad c_+(x) + c_-(x) = \frac{1}{2}\lambda^2 E(x)^2 - (\Phi_+ + \Phi_-)x + B$$

Then

$$c_+{}'(x) - c_-{}'(x) = E(x)[c_+(x) + c_-(x)] - (\Phi_+ - \Phi_-)$$

which implies

$$\lambda^2 E''(x) =$$

$$\tfrac{1}{2}\lambda^2 E(x)^3 - \{(\Phi_+ + \Phi_-)x - B\}\, E(x) - (\Phi_+ - \Phi_-)$$

— a form of Painlevé II.

For the preceding BV problem,

$$\lambda^2 E''(x) = \tfrac{1}{2}\lambda^2 E(x)^3$$

$$- \left\{ (\Phi_+ + \Phi_-)x - 2c_0 + \tfrac{1}{2}\lambda^2 E(0)^2 \right\} E(x) - (\Phi_+ - \Phi_-)$$

subject to $E'(0) = 0 = E'(1)$, with

$$\Phi_+ + \Phi_- = 2(c_0 - c_1) + \tfrac{1}{2}\lambda^2[E(1)^2 - E(0)^2]$$

$$\alpha_+\Phi_+ - \alpha_-\Phi_- = J_0$$

$$PII: \quad y''(x) = 2y(x)^3 + xy(x) + C$$

Bäcklund transformation:

$$\hat{y}(x) = -y(x) - (2C+1)/[2y'(x) + 2y(x)^2 + x]$$

$$\hat{C} = C + 1 \quad (\text{Here} \quad C \neq -1/2)$$

Inverse transformation:

$$y(x) = -\hat{y}(x) - (2\hat{C}-1)/[-2\hat{y}'(x) + 2\hat{y}(x)^2 + x]$$

$$C = \hat{C} - 1 \quad (\text{Here} \quad \hat{C} \neq 1/2)$$

Bäcklund transformation $\mathcal{B}$:

$$\hat{c}_+(x) = c_-(x) - 2\lambda^2\Phi_+ E(x)/c_+(x) + 2\lambda^2{\Phi_+}^2/c_+(x)^2$$

$$\hat{c}_-(x) = c_+(x)\,, \quad \hat{E}(x) = -E(x) + 2\Phi_+/c_+(x)$$

$$\hat{\Phi}_+ = 2\Phi_+ + \Phi_-\,, \quad \hat{\Phi}_- = -\Phi_+$$

Inverse transformation $\mathcal{B}^{-1}$:

$$c_-(x) = \hat{c}_+(x) + 2\lambda^2\hat{\Phi}_- \hat{E}(x)/\hat{c}_-(x) + 2\lambda^2\hat{\Phi}_-^2/\hat{c}_-(x)^2$$

$$c_+(x) = \hat{c}_-(x)\,, \quad E(x) = -\hat{E}(x) - 2\hat{\Phi}_-/\hat{c}_-(x)$$

$$\Phi_+ = -\hat{\Phi}_-\,, \quad \Phi_- = 2\hat{\Phi}_- + \hat{\Phi}_+$$

From any solution $\mathcal{S}^{(0)} = (c_+^{(0)}\,, c_-^{(0)}\,, E^{(0)}\,, \Phi_+^{(0)}\,, \Phi_-^{(0)})$

we construct the sequence of solutions

$$\mathcal{S}^{(n)} = \mathcal{B}^n(\mathcal{S}^{(0)}) = (c_+^{(n)}\,, c_-^{(n)}\,, E^{(n)}\,, \Phi_+^{(n)}\,, \Phi_-^{(n)})$$

for $n = 0\,, \pm 1\,, \pm 2\,, \ldots$

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Starting with Planck's exact solution as $\mathcal{S}^{(0)}$, we get a sequence of exact (rational) solutions. For example, with

$$c_{\pm}^{(0)}(0) = 1/3\,, \quad c_{\pm}^{(0)}(1) = 2/3\,, \quad \lambda = 0.1$$

we get :

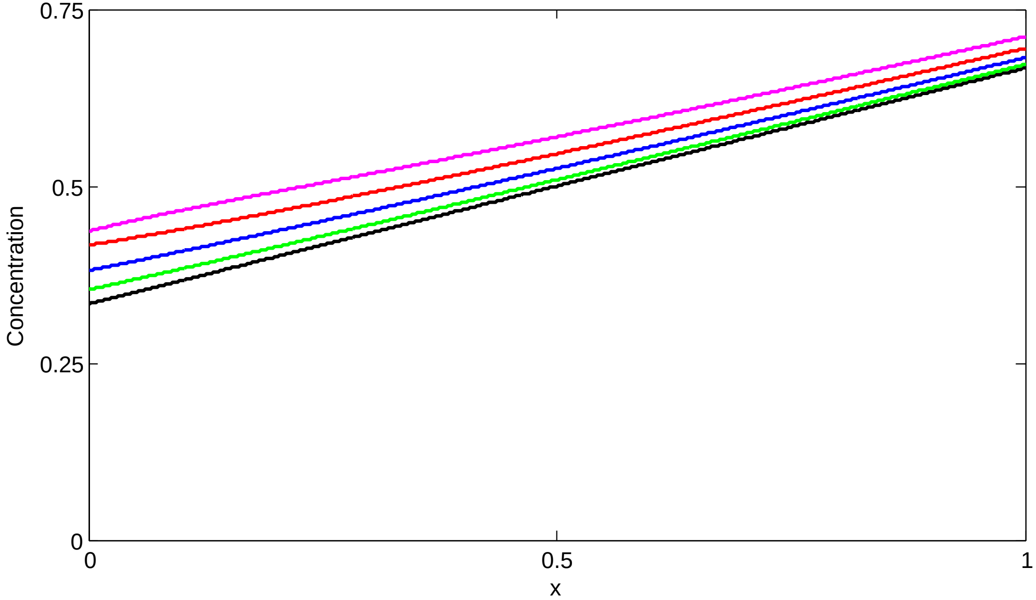

Figure 1: Graphs of $c_+^{(n)}(x)$ for $n = 0, 1, 2, 3, 4$, from bottom to top.

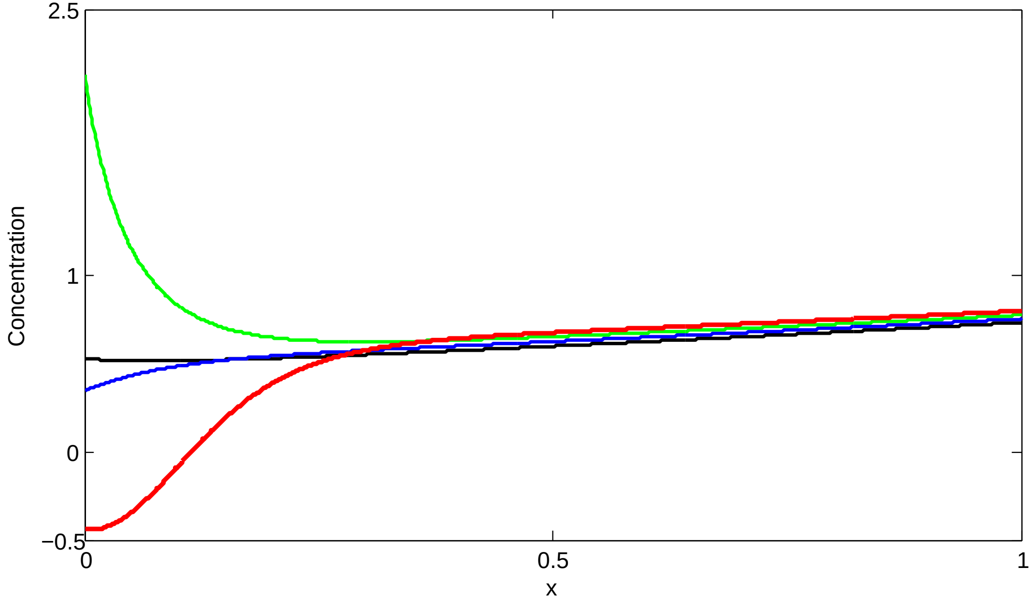

Figure 2: Graphs of $c_+^{(n)}(x)$ for $n = 5\,, 6\,, 7\,, 8$.

For the solution $\mathcal{S}^{(n)}$ we have

$$\Phi_+^{(n)} = (n+1)\Phi_+^{(0)} + n\Phi_-^{(0)}\,, \quad \Phi_-^{(n)} = -(n-1)\Phi_-^{(0)} - n\Phi_+^{(0)}$$

and hence

$$J^{(n)} = J^{(0)} + n\Delta J\,, \quad \Delta J = (\Phi_+^{(0)} + \Phi_-^{(0)})$$

— flux-quantization by Bäcklund transformations.

Physical interpretation

In dimensional form:

$$J^{(n)} = ze\left(\Phi_+^{(n)} - \Phi_-^{(n)}\right) = J_+^{(n)} + J_-^{(n)}, \text{ say}\,.$$

$$J^{(n)} = J^{(0)} + n\Delta J\,, \quad \Delta J = ze(D_+ + D_-)\left(\frac{\Phi_+^{(0)}}{D_+} + \frac{\Phi_-^{(0)}}{D_-}\right)$$

To simplify the discussion take $D_+ = D_- = D$; then

$$\Phi_+^{(0)} = \Phi_-^{(0)} = D(c_0 - c_1)/\delta$$

$$J_+^{(0)} = -J_-^{(0)} = zeD(c_0 - c_1)/\delta\,,$$

$$J^{(0)} = 0\,, \quad \Delta J = 4zeD(c_0 - c_1)/\delta\,.$$

and then

$$J_+^{(n)} = (2n + 1)\, ze\, D\, (c_0 - c_1)/\delta$$

$$J_-^{(n)} = (2n - 1)\, ze\, D\, (c_0 - c_1)/\delta$$

$$J^{(n)} = 0 + n\Delta J = 4n\, ze\, D\, (c_0 - c_1)/\delta$$

Consider the "number" of ions transported across area $\mathcal{A}$ in a time τ.

For the "state" $\mathcal{S}^{(n)}$, we have

$$n_+ = \Phi_+^{(n)} \mathcal{A}\,\tau\,, \quad n_- = \Phi_-^{(n)} \mathcal{A}\,\tau$$

so, in the "ground state" $\mathcal{S}^{(0)}$,

$$n_+ = n_- = D(c_0 - c_1)\mathcal{A}\tau/\delta$$

Consider $\mathcal{A}$ such that $n_+ = n_- \approx 1$

$$\Longrightarrow \quad \mathcal{A} \approx \delta / D(c_0 - c_1)\tau$$

[In the state $\mathcal{S}^{(0)}$, transport is purely diffusional, since $E^{(0)}(x) = 0$, so $\tau \approx \delta^2/2D$, and hence

$$\mathcal{A} \approx 2/(c_0 - c_1)\delta \, .]$$

Then, for this same area $\mathcal{A}$ and time τ,

$$J_+^{(n)}\mathcal{A}\tau = (2n+1)ze\,, \quad J_-^{(n)}\mathcal{A}\tau = (2n-1)ze$$

$$J^{(n)}\mathcal{A}\tau = 4nze$$

Then, for this same area $\mathcal{A}$ and time τ,

$$J_{+}^{(n)} \mathcal{A}\tau = (2n+1)ze\,, \quad J_{-}^{(n)} \mathcal{A}\tau = (2n-1)ze$$

$$J^{(n)} \mathcal{A}\tau = 4nze$$

Thus: In the state $\mathcal{S}^{(0)}$:

One positive ion diffuses across $\mathcal{A}$ in time τ in $+x$-direction.

One negative ion diffuses across $\mathcal{A}$ in time τ in $+x$-direction.

Zero net charge across $\mathcal{A}$ in time τ. ($J^{(0)} \mathcal{A}\tau = 0$)

In the state $\mathcal{S}^{(1)}$:

$$J_+^{(1)} = 3ze\,, \quad J_-^{(1)} = ze$$

Three positive ions across $\mathcal{A}$ in time τ in $+x$-direction.

One negative ion across $\mathcal{A}$ in time τ in $-x$-direction.

Net charge across $\mathcal{A}$ in time τ in $+x$-direction equals $4ze$.

In the state $\mathcal{S}^{(-1)}$:

$$J_+^{(1)} = -ze\,, \quad J_-^{(1)} = -3ze$$

One positive ion across $\mathcal{A}$ in time τ in $-x$-direction.

Three negative ions across $\mathcal{A}$ in time τ in $+x$-direction.

Net charge across $\mathcal{A}$ in time τ in $+x$-direction equals $-4ze$.

In the state $\mathcal{S}^{(-1)}$:

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One positive ion across $\mathcal{A}$ in time τ in $-x$-direction.

Three negative ions across $\mathcal{A}$ in time τ in $+x$-direction.

Net charge across $\mathcal{A}$ in time τ in $+x$-direction equals $-4ze$.

— and so on.

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- Note that flux-quantization persists no matter how small λ is (so long as it is non-zero!).

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$$c_-(x) = \hat{c}_+(x) + 2\lambda^2\hat{\Phi}_-\, \hat{E}(x)/\hat{c}_-(x) + 2\lambda^2\hat{\Phi}_-^2/\hat{c}_-(x)^2$$

$$c_+(x) = \hat{c}_-(x)\,, \quad E(x) = -\hat{E}(x) - 2\hat{\Phi}_-/\hat{c}_-(x)$$

$$\Phi_+ = -\hat{\Phi}_-\,, \quad \Phi_- = 2\hat{\Phi}_- + \hat{\Phi}_+$$

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