Theory of Two-Step Surface EC’EC’ Mechanism in Protein-Film Square-Wave Voltammetry

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Abstract

If two irreversible regenerative chemical reactions get associated to both electrochemically generated products of a two-step successive electrochemical surface mechanism, while causing regeneration of the initial reactant and the intermediate generated electrochemically, then the name of this mechanism in electrochemical terminology is ***EC’EC’ mechanism***. In this work, for the first time this complex mechanism is solved under conditions of square-wave voltammetry, and the entire simulation MATHCAD file is provided for free. The voltammetric patterns of this complex mechanism are function of the electron transfer coefficients related to both electron transfer steps, of the kinetics of electron transfer of both electron transfer steps, and of the kinetics of both regenerative chemical steps. Importance of this mechanism is found in the redox behavior of lipophilic redox enzymes whose electrochemical transformation occurs in two successive steps.

TWO STEP SURFACE EC'EC'cat Mechanism in SWV---new version 30 0ct 2023

$EsI := 0.25 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.064 \quad EsII := 0.65 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{.5\cdot r}$

$KII := 10^{.5}$

$j := 1..\frac{\Delta E}{dE}\cdot 50$

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$

$\log(KI_r) =$ $\boxed{0.5}$

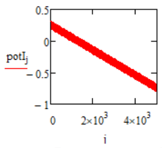
$\lambda := .884001246$

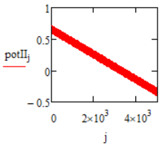
λ e kineticki parametar na regenerativna hemiska reakcija povrzana so prv elektroden cekor

$KI_1 = 3.162$

$$potI_j := EsI + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

$$potII_j := EsII + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$





$z := .28825162001$

z e kataliticki regenerativen hemiski parametar povrzan so vtor cekor

$\Phi I_j := n\cdot\frac{F}{R\cdot T}\cdot potI_j \quad \Phi II_j := n\cdot\frac{F}{R\cdot T}\cdot potII_j$

$$A_j := e^{-\lambda\cdot\frac{j}{50}} - e^{-\lambda\cdot\frac{j+1}{50}}$$

$$B_j := e^{-z\cdot\frac{j}{50}} - e^{-z\cdot\frac{j+1}{50}}$$

$$\Psi I_{1,r} := \frac{\frac{KI_r}{1}\cdot e^{-\alpha 1\cdot\Phi I_1}}{1 + KI_r\cdot\lambda^{-1}\cdot A_1\cdot e^{-\alpha 1\cdot\Phi I_1} + 1\lambda^{-1}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}\cdot A_1}$$

$$\Psi II_{1,r} := \frac{\lambda^{-1}KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{1 + \frac{KII}{\lambda}\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\left(1 + e^{\Phi II_1}\right)}\cdot\Psi I_{1,r}\cdot B_1$$

$\Psi I_{1,1} = 7.159\times 10^{-4}$

$\Psi II_{1,1} = 0$

$$\Psi I_{j,r} := \frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_j} - KI_r\cdot\frac{1}{\lambda}\cdot e^{-\alpha 1\cdot\Phi I_j}\cdot\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right) - KI_r\lambda^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha 1)}\cdot\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right)}{1 + KI_r\cdot\frac{1}{\lambda}\cdot A_1\cdot e^{-\alpha 1\cdot\Phi I_j} + \lambda^{-1}\cdot e^{\Phi I_j\cdot(1-\alpha 1)}\cdot A_1\cdot KI_r}$$

$$\Psi II_{j,r} := \frac{KII\frac{1}{\lambda}\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right) - \frac{1}{(z)}KII\cdot e^{\Phi II_j\cdot(-\alpha 2)}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot B_{j-i+1}\right) - \frac{1}{(z)}KII\cdot e^{1\cdot\Phi II_j\cdot(1-\alpha 2)}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot B_{j-i+1}\right)}{1 + \frac{1\cdot B_1}{(z)}KII\cdot e^{\Phi II_j\cdot(-\alpha 2)} + \frac{1\cdot B_1}{(z)}KII\cdot e^{\Phi II_j\cdot(1-\alpha 2)}}$$

$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$

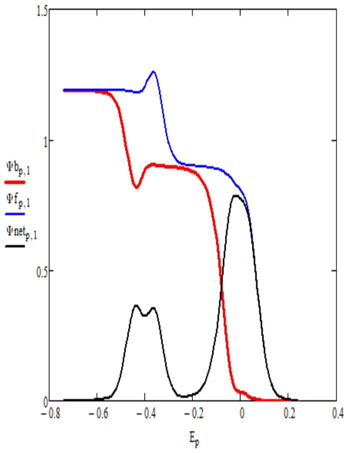
$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$

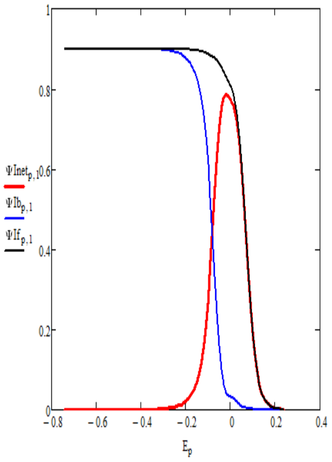
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

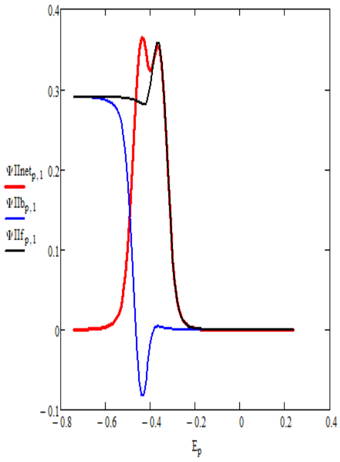
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

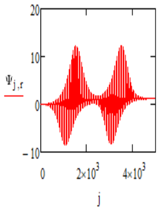
$E_p := EsI - p\cdot dE$

$\Psi b_{p,r} := \Psi_{50\cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1)\cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$









$\Psi f_{p,1} =$

$9.42\cdot 10^{-4}$
$1.387\cdot 10^{-3}$
$2.041\cdot 10^{-3}$
$3\cdot 10^{-3}$
$4.405\cdot 10^{-3}$
$6.46\cdot 10^{-3}$
$9.455\cdot 10^{-3}$
0.014
0.02

$\Psi b_{p,1} =$

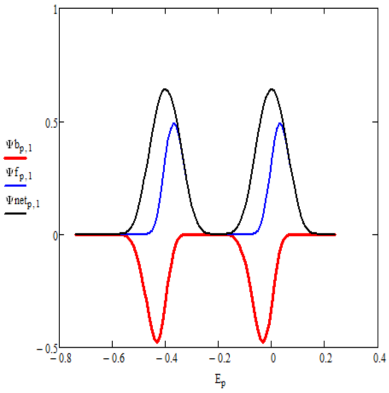
$6.517\cdot 10^{-6}$
$9.617\cdot 10^{-6}$
$1.419\cdot 10^{-5}$
$2.094\cdot 10^{-5}$
$3.09\cdot 10^{-5}$
$4.559\cdot 10^{-5}$
$6.725\cdot 10^{-5}$
$9.921\cdot 10^{-5}$
$1.463\cdot 10^{-4}$
$2.158\cdot 10^{-4}$

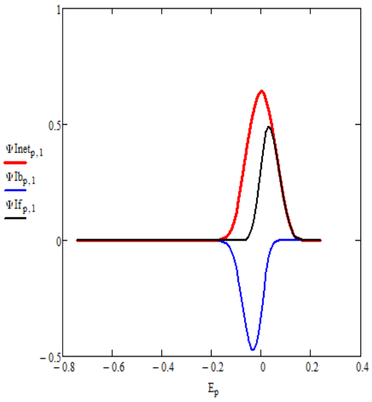
$\Psi net_{p,1} =$

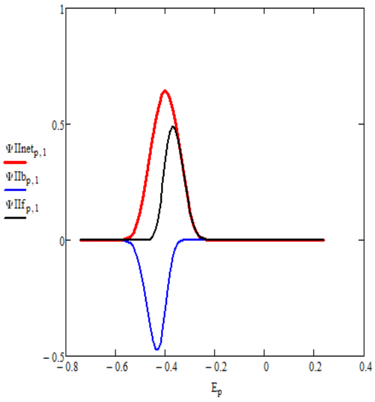
$9.355\cdot 10^{-4}$
$1.377\cdot 10^{-3}$
$2.026\cdot 10^{-3}$
$2.979\cdot 10^{-3}$
$4.374\cdot 10^{-3}$
$6.414\cdot 10^{-3}$
$9.388\cdot 10^{-3}$
0.014
0.02

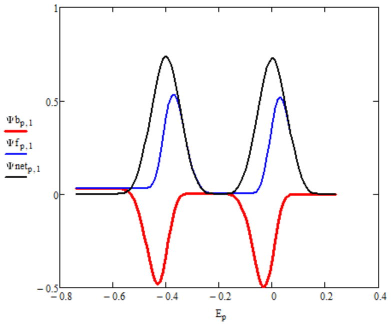
$E_p =$

0.24
0.23
0.22
0.21
0.2
0.19
0.18
0.17








1
0.5
0
−0.5
$\Psi b_{p,1}$
$\Psi f_{p,1}$
$\Psi net_{p,1}$
−0.8
−0.6
−0.4
−0.2
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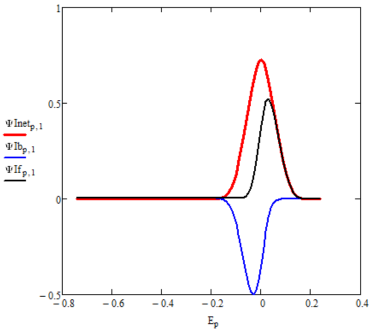
0.2
0.4
E_p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$\Psi Ib_{p,1}$
$\Psi If_{p,1}$
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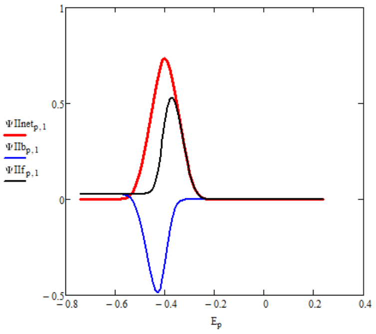
E_p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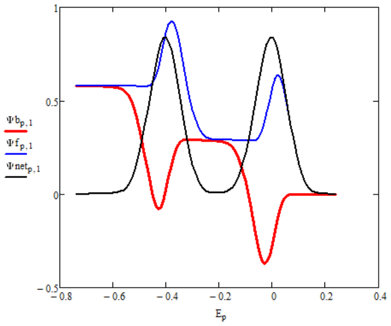
0.4
E_p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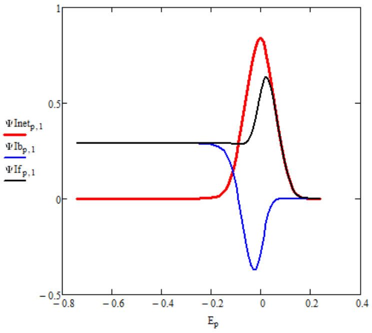
E_p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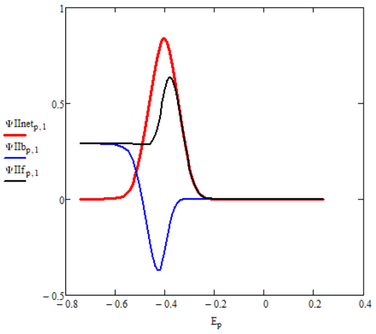
E_p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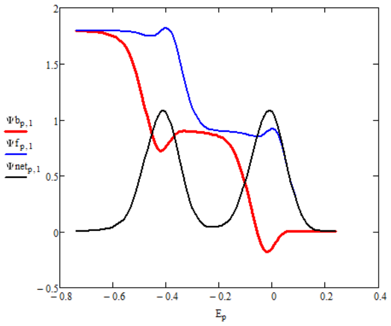
E_p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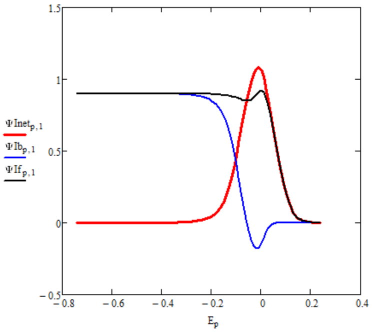
E_p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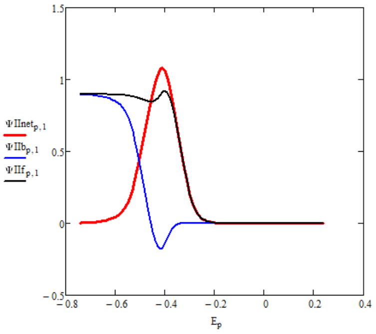
E_p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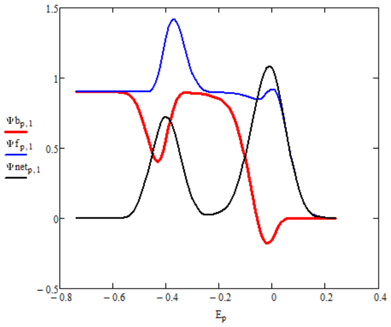
E_p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−0.2
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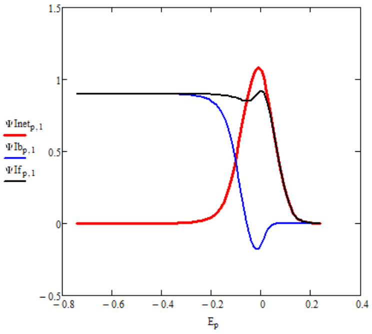
E_p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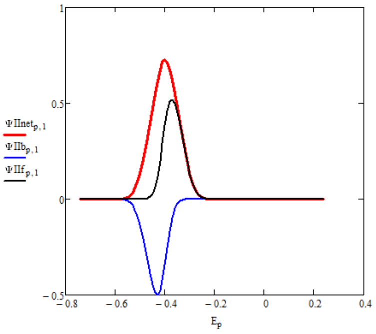
E_p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−0.4
−0.2
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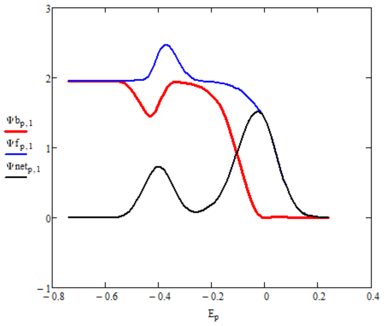
E_p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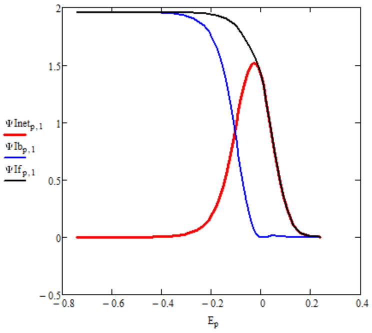
E_p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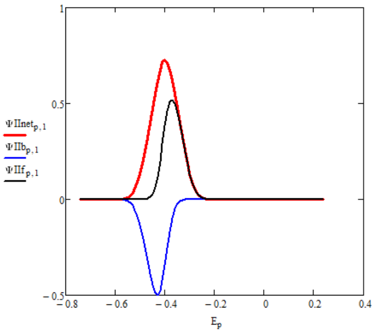
E_p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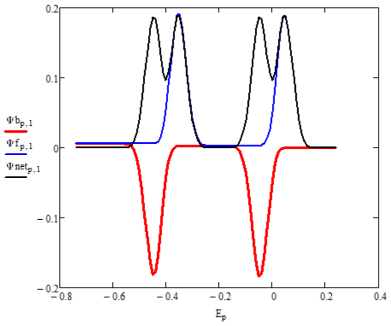
E_p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0.1
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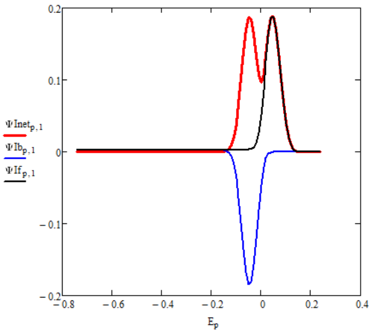
E_p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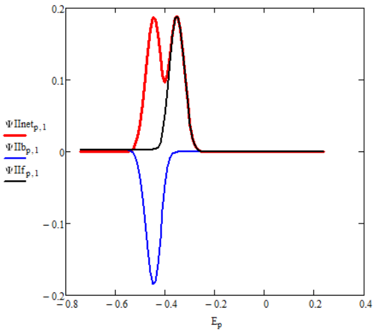
E_p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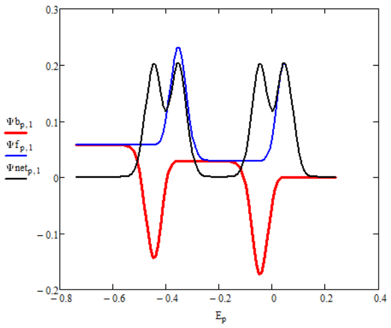
0.2
0.4
E_p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$\Psi f_{p,1}$
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0.2
0.1
0
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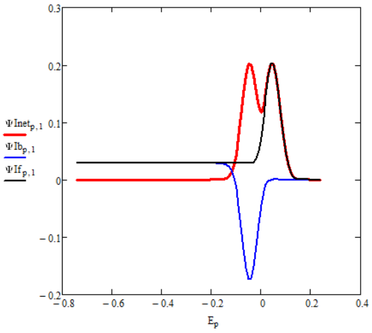
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p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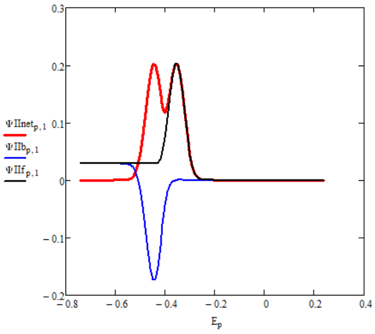
E_p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−0.8
−0.6
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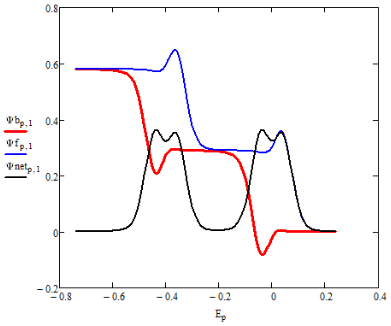
0.4
E_p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0.6
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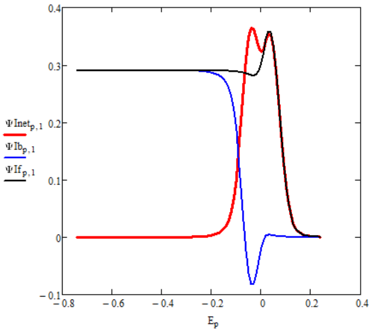
0.2
0.4
E_p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0.4
0.3
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−0.6
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−0.2
0
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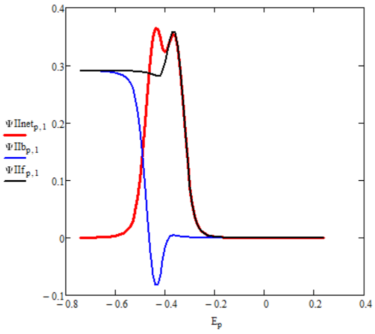
0.4
E_p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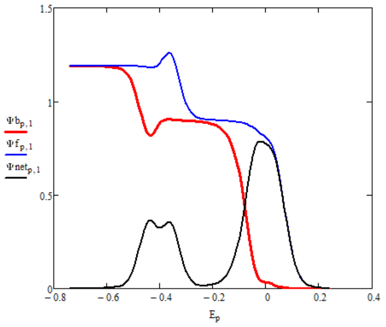
0.4
E_p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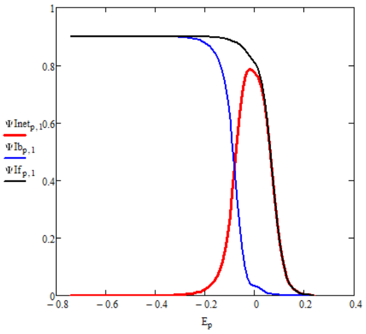
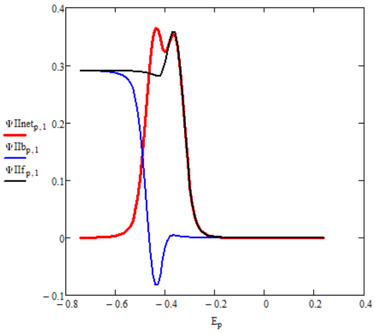
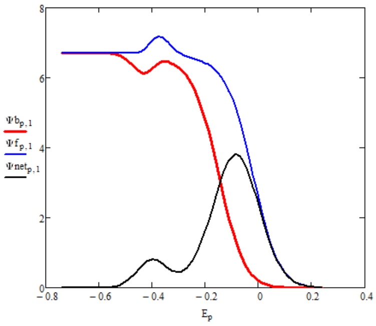
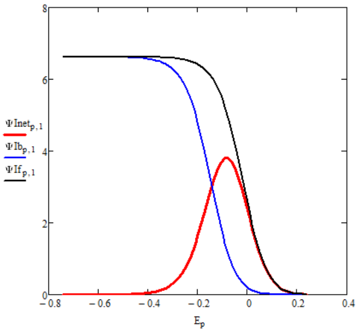
−0.2
0
0.2
0.4
E_p


$\Psi Inet_{p,1}$
$\Psi Ib_{p,1}$
$\Psi If_{p,1}$
1
0.8
0.6
0.4
0.2
0
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p

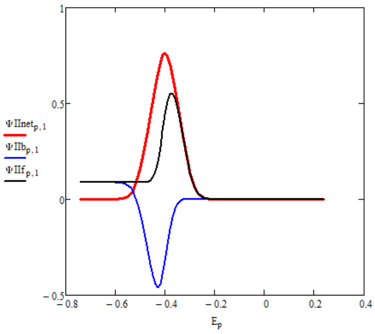

$\Psi IInet_{p,1}$
$\Psi IIb_{p,1}$
$\Psi IIf_{p,1}$
0.4
0.3
0.2
0.1
0
−0.1
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p



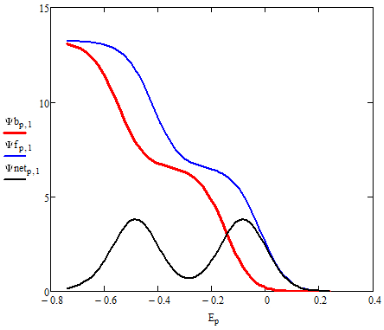
8
6
4
2
0
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p
$\Psi b_{p,1}$
$\Psi f_{p,1}$
$\Psi net_{p,1}$



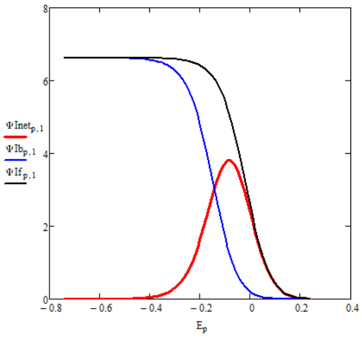
8
6
4
2
0
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p
$\Psi Inet_{p,1}$
$\Psi Ib_{p,1}$
$\Psi If_{p,1}$



1
0.5
0
−0.5
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p
$\Psi IInet_{p,1}$
$\Psi IIb_{p,1}$
$\Psi IIf_{p,1}$



15
10
5
0
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p
$\Psi b_{p,1}$
$\Psi f_{p,1}$
$\Psi net_{p,1}$



8
6
4
2
0
−0.8
−0.6
−0.4
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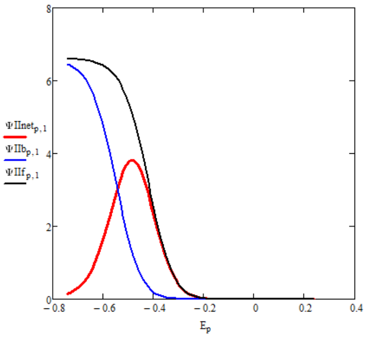
0
0.2
0.4
E_p
$\Psi Inet_{p,1}$
$\Psi Ib_{p,1}$
$\Psi If_{p,1}$



8
6
4
2
0
−0.8
−0.6
−0.4
−0.2
0
0.2
0.4
E_p
$\Psi IInet_{p,1}$
$\Psi IIb_{p,1}$
$\Psi IIf_{p,1}$

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