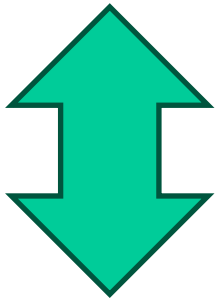
How to solve equations?

Self-consistent method

自己無撞着法

Problems whose final unique solution is obtained just by one step calculation

- **Linear least-squares method**
- **Up to 4th order polynomial equations**



Five or higher order polynomial,
Transcendental equation (超越方程式)

- Difficult to have an analytical solution
- Even numerical analysis cannot give final solution by one-cycle calculation

＝＞ Iterative calculation (反復計算)

Simplest method: Self-consistent (SC) method

A simple case: Solve $g(x) = 0$

SC method is applicable by converting to $x = g(x) + x = f(x)$

Note: not efficient nor stable for many cases

Simple procedure:

Initial value x_0

1st iteration : $x_1 = f(x_0)$

2nd iteration: $x_2 = f(x_1)$ ….

Difficult to converge: Diverge, Oscillation

(収束しにくい: 発散、振動)

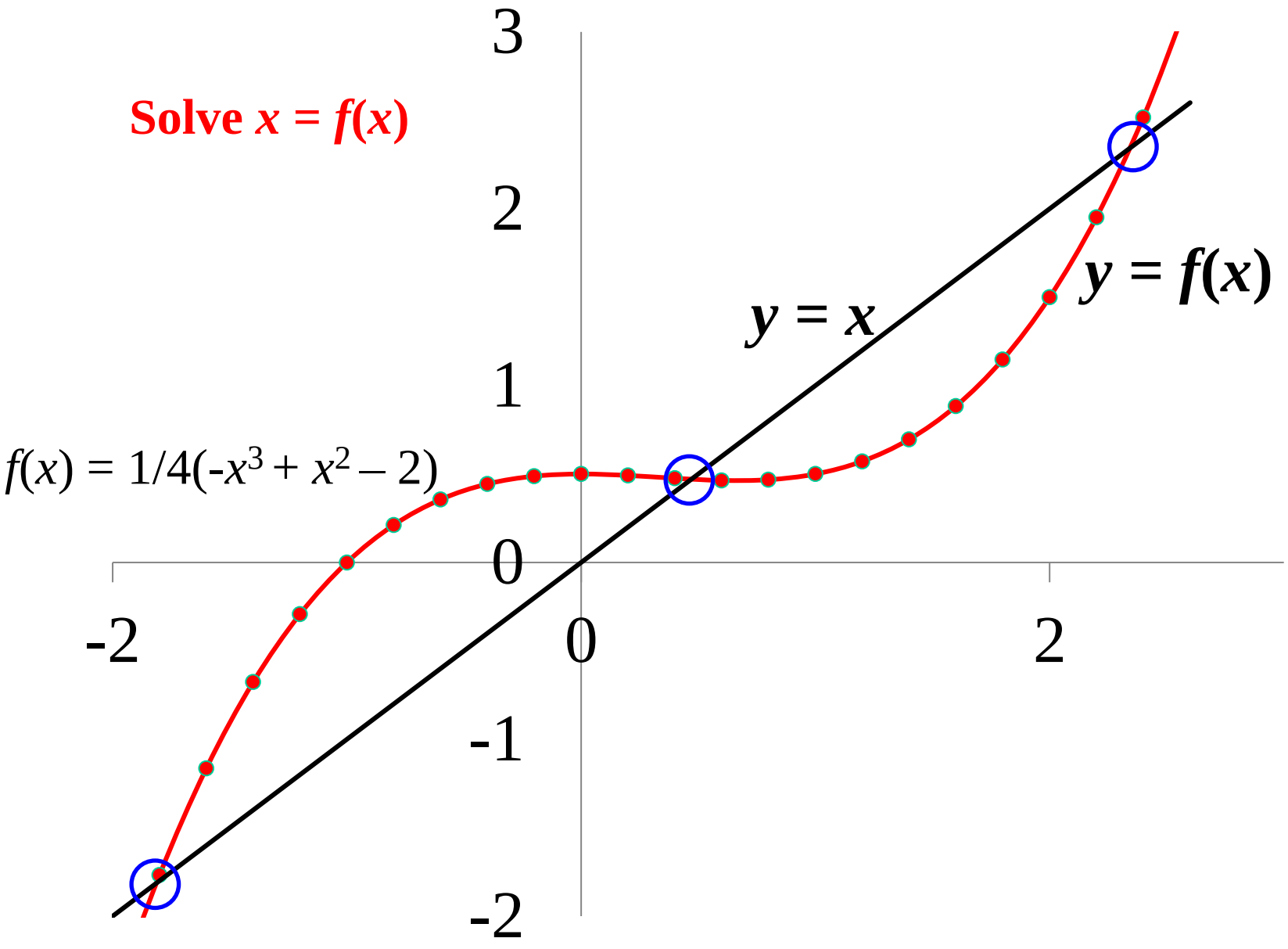
Mixing factor (混合係数) **k_{mix}: Stabilize convergence**

Initial value x_0

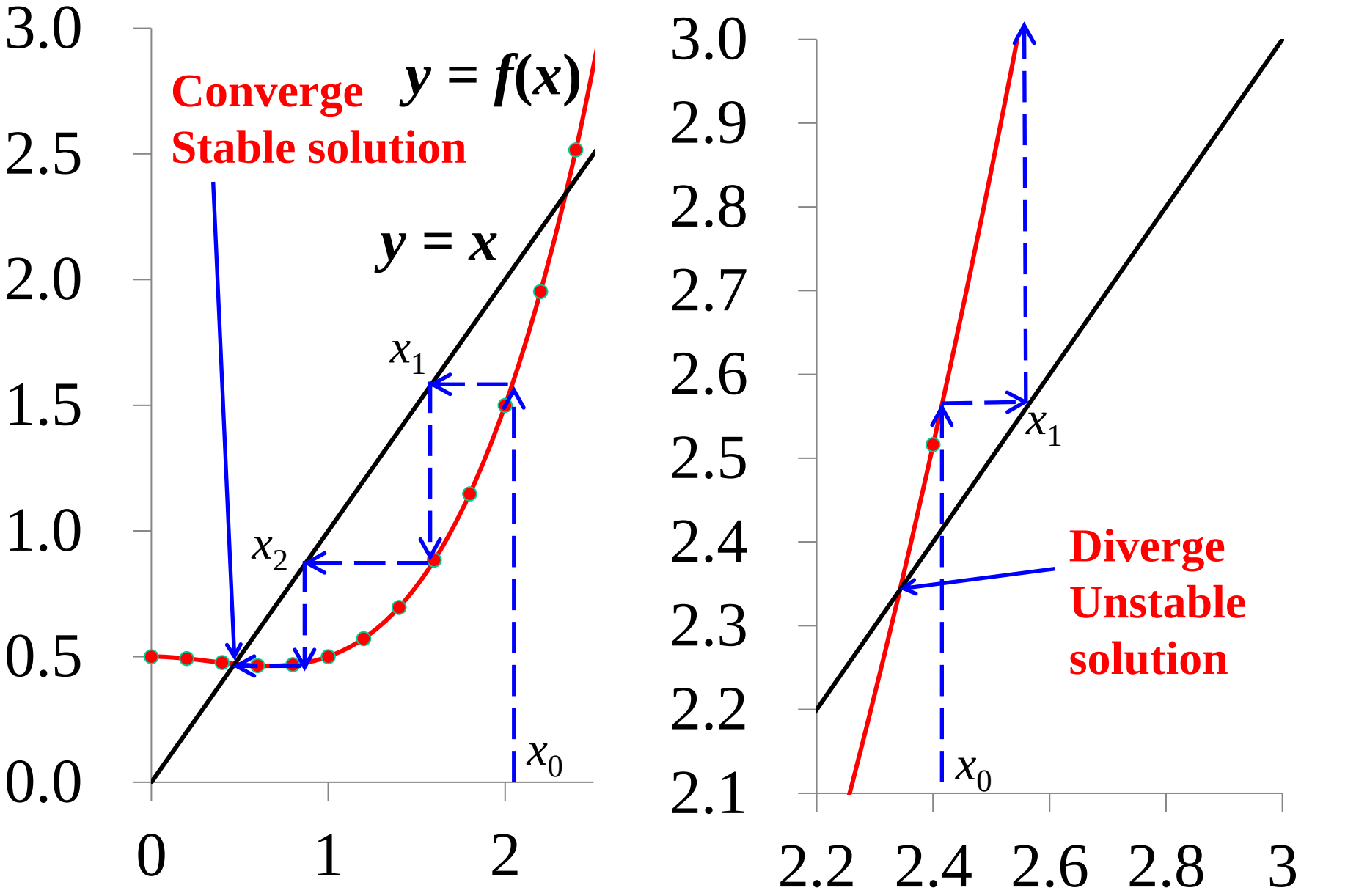
1st iteration : $x_1 = f(x_0)$ => $x_1' = (1 - k_{mix})\, x_0 + k_{mix} x_1$

2nd iteration: $x_2 = f(x_1')$ ….

Illustrative explanation of SC



SC: Convergence process



$|f'(x)| < 1$ must be satisfied for convergence

Example of SC: Diode with series resistance

$$I = I_0\left[\exp\left(\frac{e}{nkT}(V - RI)\right) - 1\right]$$

Repeat

$$I_i = I_0\left[\exp\left(\frac{e}{nkT}(V - RI_{i-1})\right) - 1\right]$$

until abs($I_i - I_{i-1}$) < EPS is achieved

- E.g., initial voltages would be chosen as $V/2$ for the diode and the R
- This SC is not so stable; mixing factor k should be adjusted

For sequential calculations of $I - V$ characteristic, e.g., V from 0.0 to 1.0, using a preconverged result for the initial value of the next V will enhance convergence.

例えばVを順次変えてI-V特性を計算するような場合、すでに収束した値を次のVにおける初期値として利用すると早く収束できる。

SC-Diode.xlsx

i	I	Ical	|error|	I0=	1.E-12	A
0	2	-1E-12	2	n=	1	
1	1.8	-1E-12	1.8	T=	300	K
2	1.62	-1E-12	1.62	R=	1	ohm
3	1.458	-1E-12	1.458	V=	1	
4	1.3122	-1E-12	1.3122			
5	1.18098	-1E-12	1.18098	k=	0.1	
6	1.062882	-9.1E-13	1.06288			
7	0.956594	4.31E-12	0.95659			
8	0.860934	2.09E-10	0.86093			
9	0.774841	5.77E-09	0.77484			
10	0.697357	1.14E-07	0.69736			
11	0.627621	1.66E-06	0.62762			
12	0.564859	1.86E-05	0.56484			
13	0.508375	0.000163	0.50821			
14	0.457554	0.00115	0.4564			
15	0.411914	0.006655	0.40526			
16	0.371388	0.031631	0.33976			
17	0.337412	0.116849	0.22056			
18	0.315356	0.272927	0.04243			
19	0.311113	0.321305	0.01019			
20	0.312132	0.308953	0.00318			
21	0.311814	0.312754	0.00094			
22	0.311908	0.311626	0.00028			
23	0.31188	0.311965	8.5E-05			
24	0.311888	0.311863	2.5E-05			
25	0.311886	0.311893	7.6E-06			
26	0.311887	0.311884	2.3E-06			

First-principles calculation :

Self-consistent field (SCF,自己無撞着) calculation

- Hamiltonian of one-electron quantum equation includes wave functions

$$\left\{-\frac{1}{2}\nabla_l - \sum_m \frac{Z_m}{r_{lm}} + \sum_m \int \frac{\rho_m(\mathbf{r}_m)}{r_{lm}} d\mathbf{r}_m + V_{Xl}(\mathbf{r}_l)\right\}\phi_l(\mathbf{r}_l) = \varepsilon_l \phi_l(\mathbf{r}_l)$$

- First-step calculation requires electron density guessed / assumed ρ_{ini} :
  e.g,. by uniform density, sum of atomic electron density,,,

- Electron density ρ_{fin} is calculated the solved wave functions, but ρ_{fin} would be different from ρ_{ini}

ρ_{ini} must be equal to ρ_{fin}, otherwise these loss physical meaning

- More appropriate ρ_{new} is guessed from ρ_{fin} and ρ_{ini}, and repete the above calculations

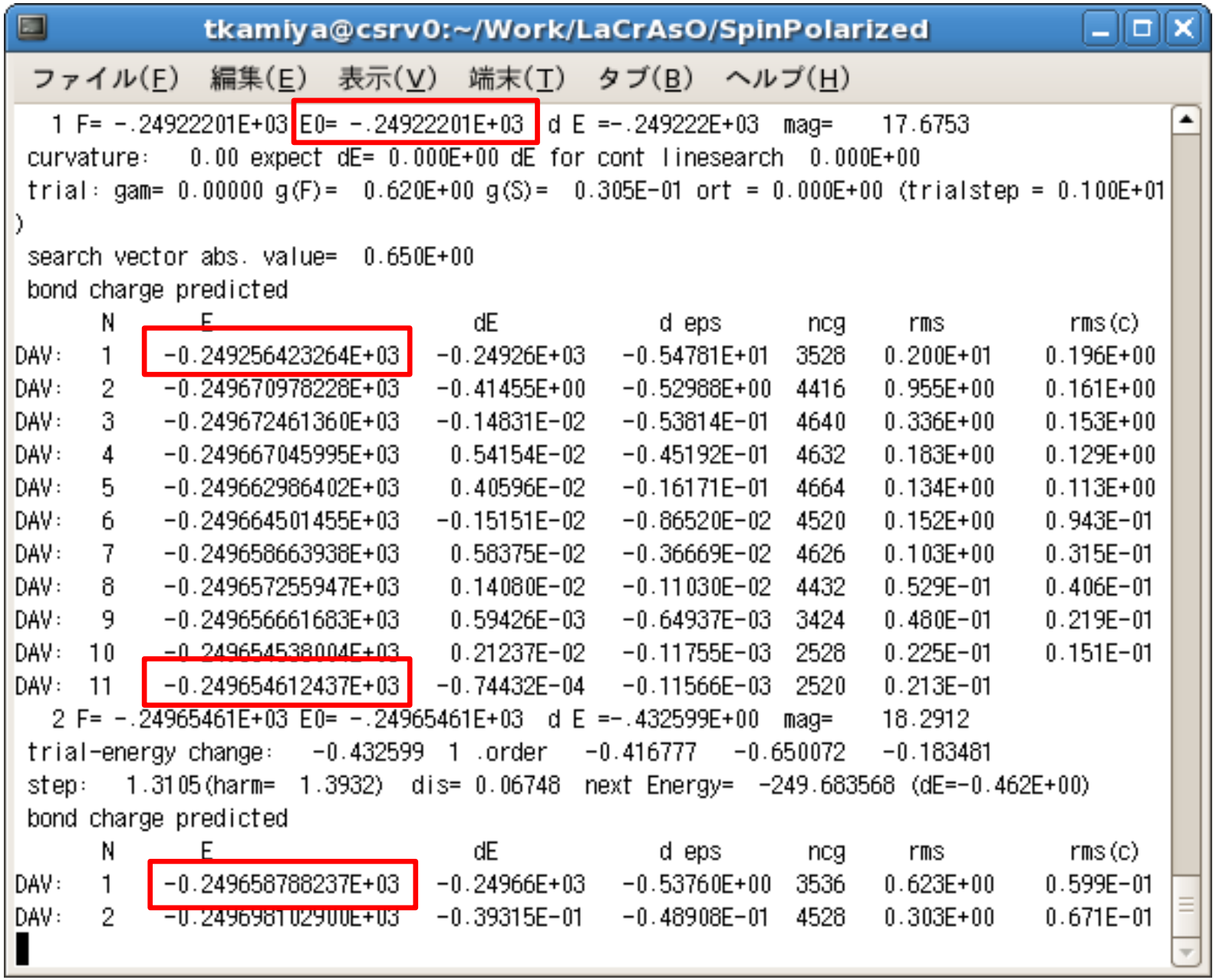
  ex. : $\rho_{new} = \rho_{ini} + k_{mix}(\rho_{fin} - \rho_{ini})$

  k_{mix} : Mixing factor

  A parameter to suppress divergence of the SCF calculation
  close to 1 would be easily diverged, close to 0 causes slow convergence

SCF cycle
Repeat until $\rho_{fin} = \rho_{ini}$

Example: SCF/structure relaxation by VASP



Typical iteration of SC calculation

Find the solution of $f(x, \rho(x)) = 0$:

Case this is easily done if $\rho(x)$ is provided

1. Assume $\rho(x)$ and solve $f(x, \rho(x)) = 0$ to get approximate x_i
2. Calculate $\rho(x_i)$ with the obtained x_i, solve $f(x, \rho(x_i)) = 0$, and get improved approximation x_{i+1}
3. Repeat 1 – 2 so as to decrease $|\rho(x_{i+1}) - \rho(x_i)|$, $|x_{i+1} - x_i|$ to required accuracy

Self-consistent approach (自己無動着計算)

May be diverged if the obtained x_i' is used for x_{i+1}

=> **Stabilize convergece using mixing factor** (混合係数) k_{mix}

Initial x_0

First iteration: $x_1 = f(x_0)$ => $x_1' = (1 - k_{mix})\, x_0 + k_{mix} x_1$

Next iteration: $x_2 = f(x_1')$ ….

Problems of SC calculations

- **Some solutions would not be obtained** (収束しない解があり得る)

  $f'(x) < 1$ must be satisfied at the solution to obtain the solution of $x = f(x)$

  => Conversion of the equation may help, but not always

- **Convergence is not stable**

  mixing factor may improve

For many cases, use another method such as Newton method

- **Cases SC method is effective**

  Initial values close to the solution

  Effect of SC parameters is small to the equation

  (自己無撞着変数の方程式への影響が小さい)

  SC parameters have good convergence

  (自己無撞着変数の収束特性が良く、予測できる場合)

How to solve equations?

More sophisticated algorithms

Newton-Raphson method

Solve $f(x) = 0$

Start from initial guess: x_0

x_0+dx is supposed to be a solution

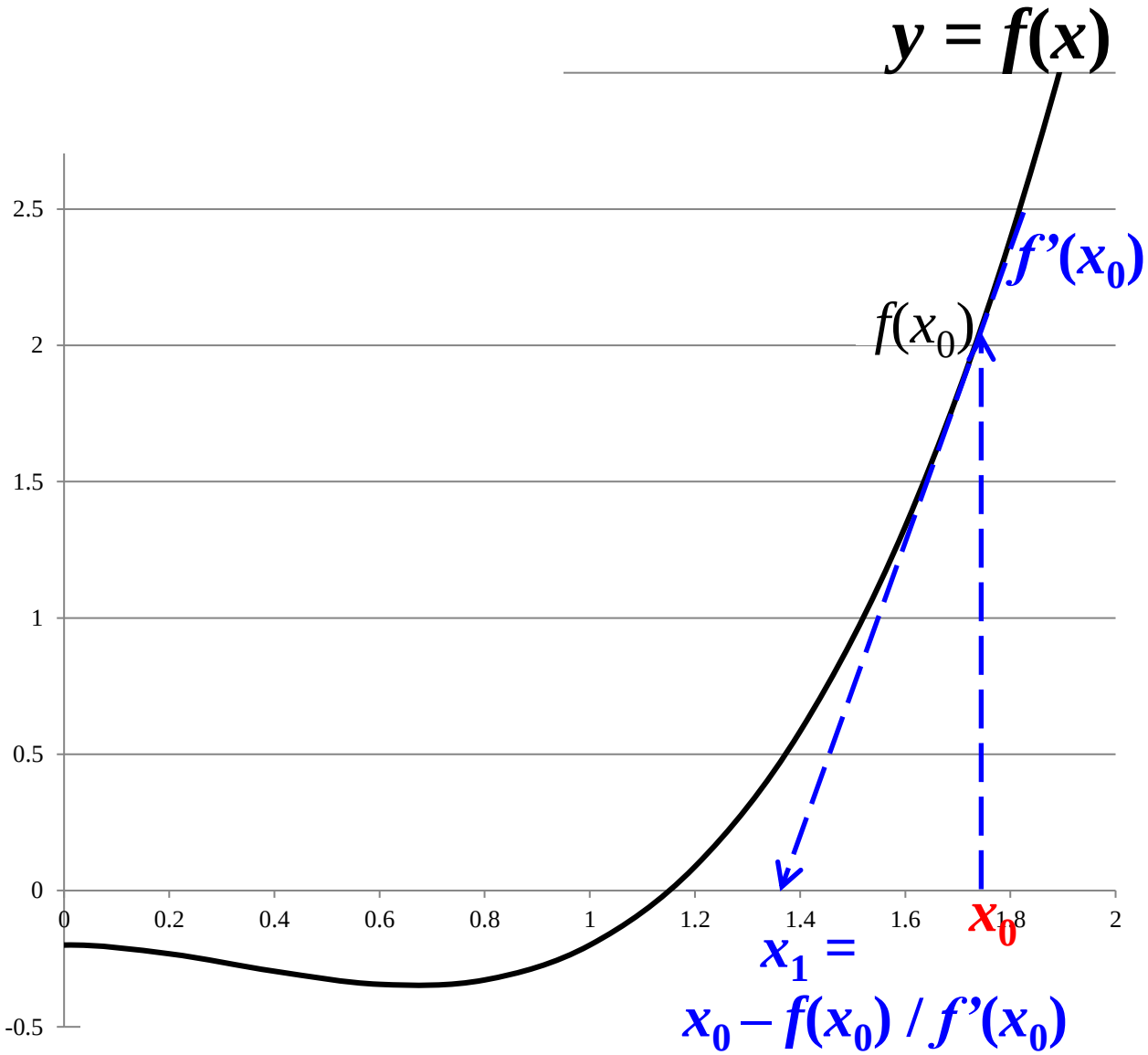
$$f(x_0+dx) = f(x_0) + dx\, f'(x_0) \sim 0$$

$$\Rightarrow \quad x_1 = x_0 + dx = x_0 - f(x_0) / f'(x_0)$$

Stabilize convergence:

$$x_{k+1} = x_k - f(x_k) / f'(x_k) / (1 + \lambda)$$

λ: Dumping Factor



Program: equation-newton-Raphson.py

Usage: python equation-newton-raphson.py x0 dump t_{sleep}

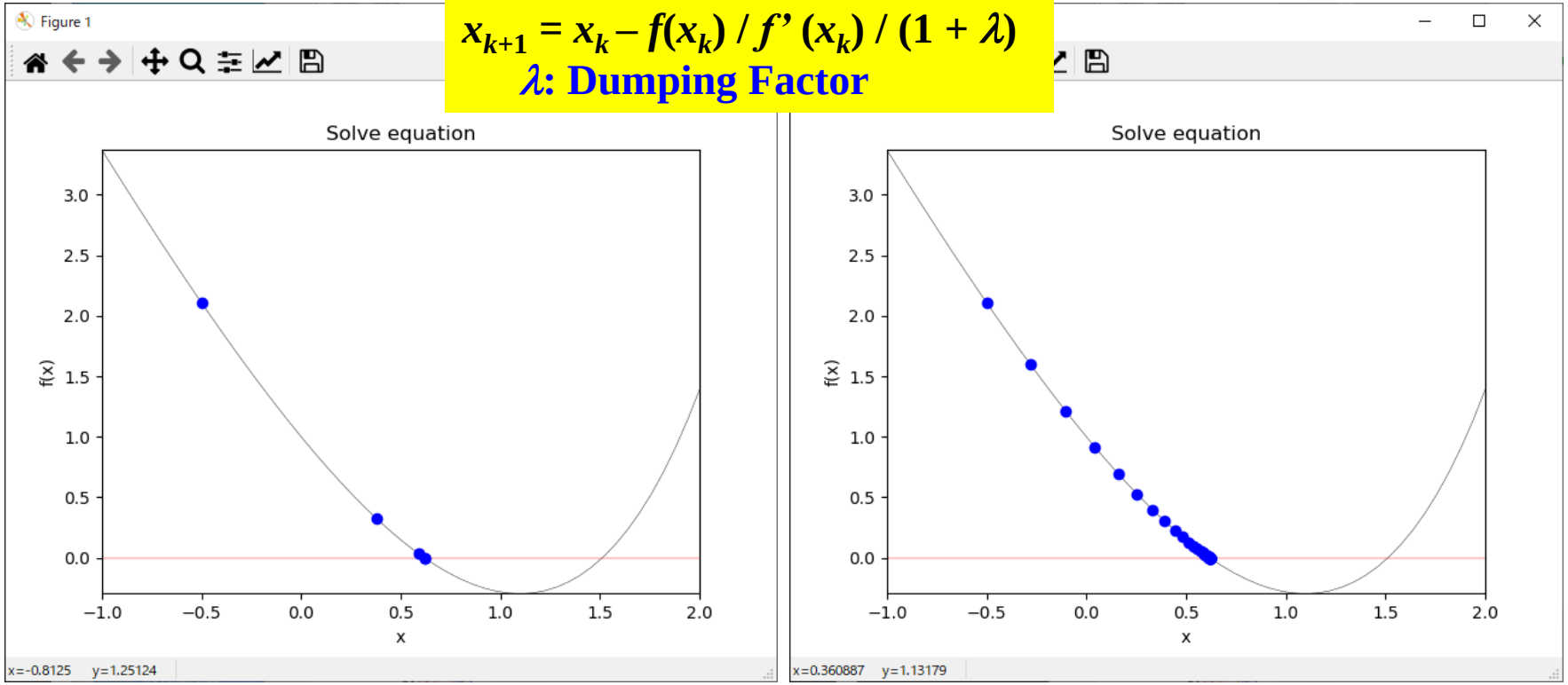
$f(x) = \exp(x) - 3.0x$

python equation-newton-raphson.py -0.5 0

python equation-newton-raphson.py -0.5 3

$$x_{k+1} = x_k - f(x_k) / f'(x_k) / (1 + \lambda)$$

λ: Dumping Factor

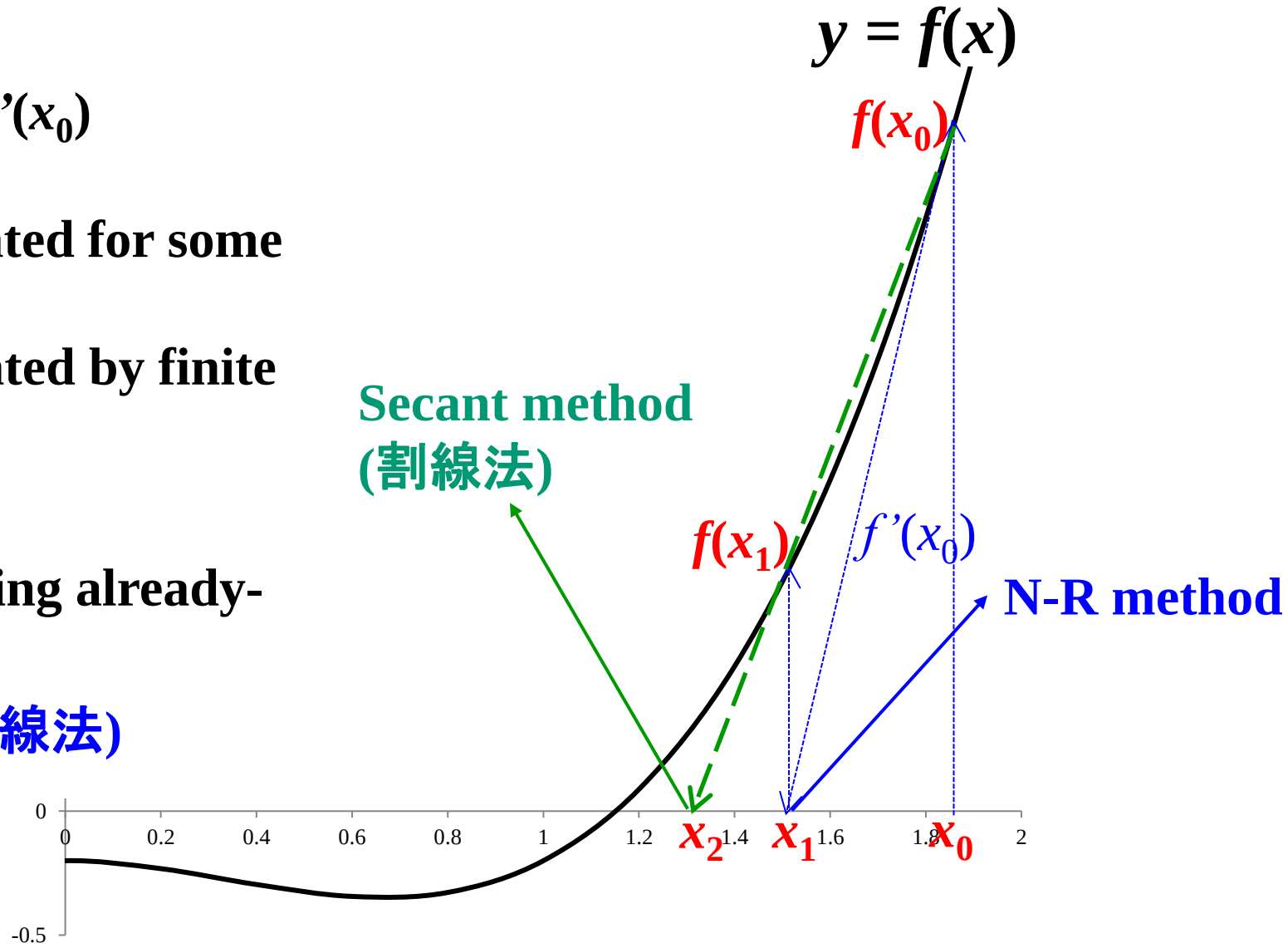


Newton-Raphson method / Secant method

Solve $f(x) = 0$

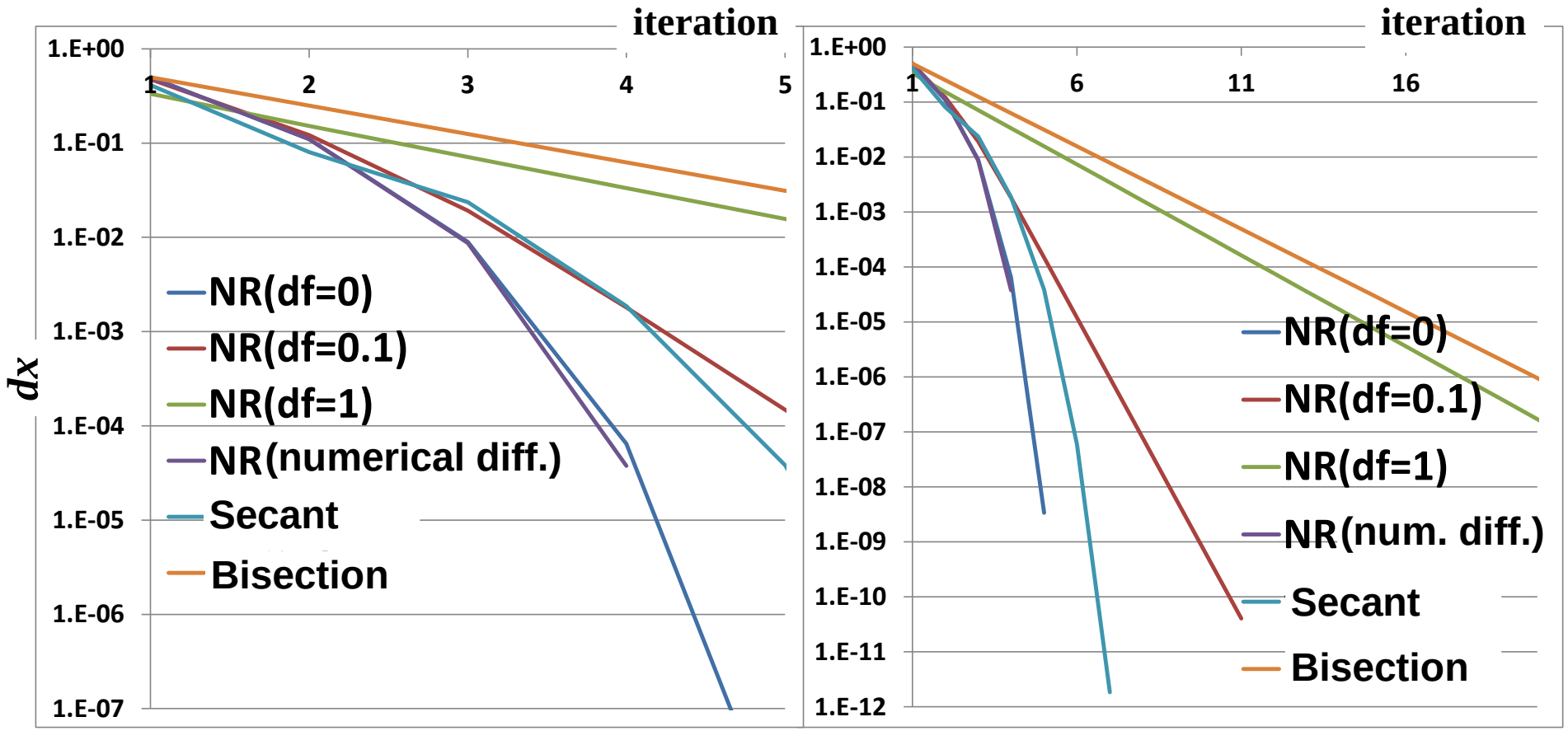
Start from initial guess: x_0
repeat: $x_1 = x_0 + dx = x_0 - f(x_0) / f'(x_0)$

- **$f'(x_0)$ can be analytical calculated for some cases**
- **$f'(x_0)$ is more often approximated by finite difference**
  $\frac{f(x_0+h)-f(x_0-h)}{2h}$
- **$f'(x_0)$ can be approximated using already-calculated values**
  $\frac{f(x_1)-f(x_0)}{x_1-x_0}$ **Secant method (割線法)**



Effect of dumping factor: Convergence process

$f(x) = \exp(x) - 3x = 0$ (initial $x = 0$) Exact 0.619061



$x_{k+1} = x_k - f(x_k) / (f'(x_k) + \lambda)$

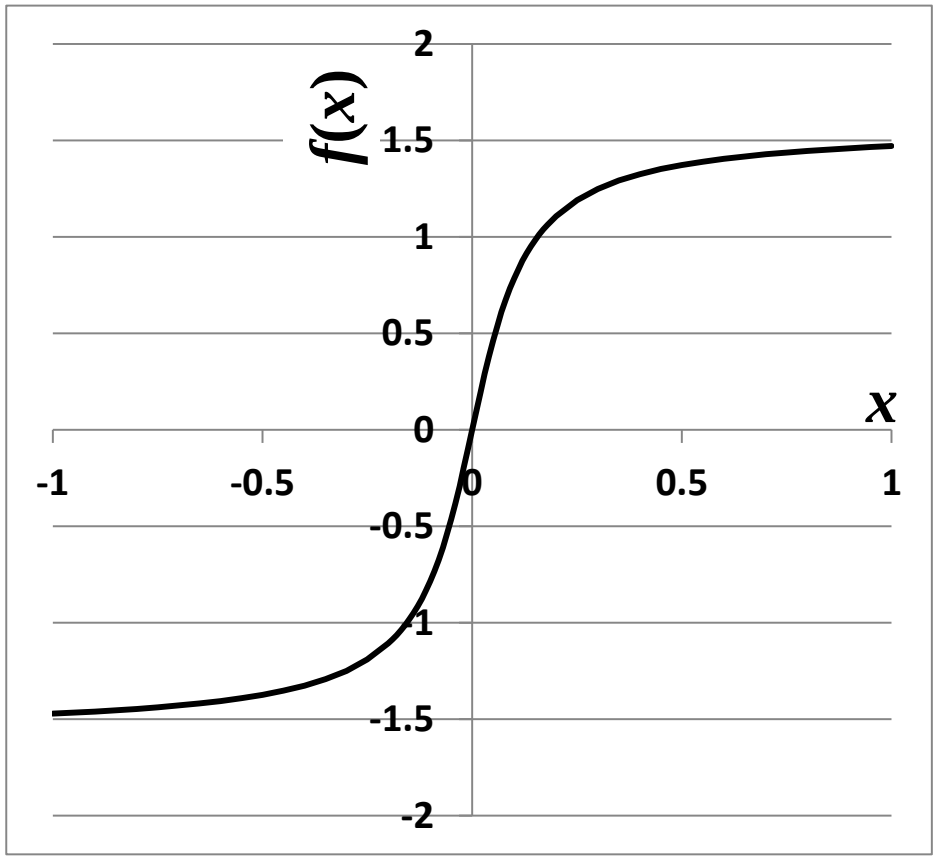
λ: Dumping Factor

NR: Newton-Raphson method
df: Dumping Factor

Case Newton method succeeds

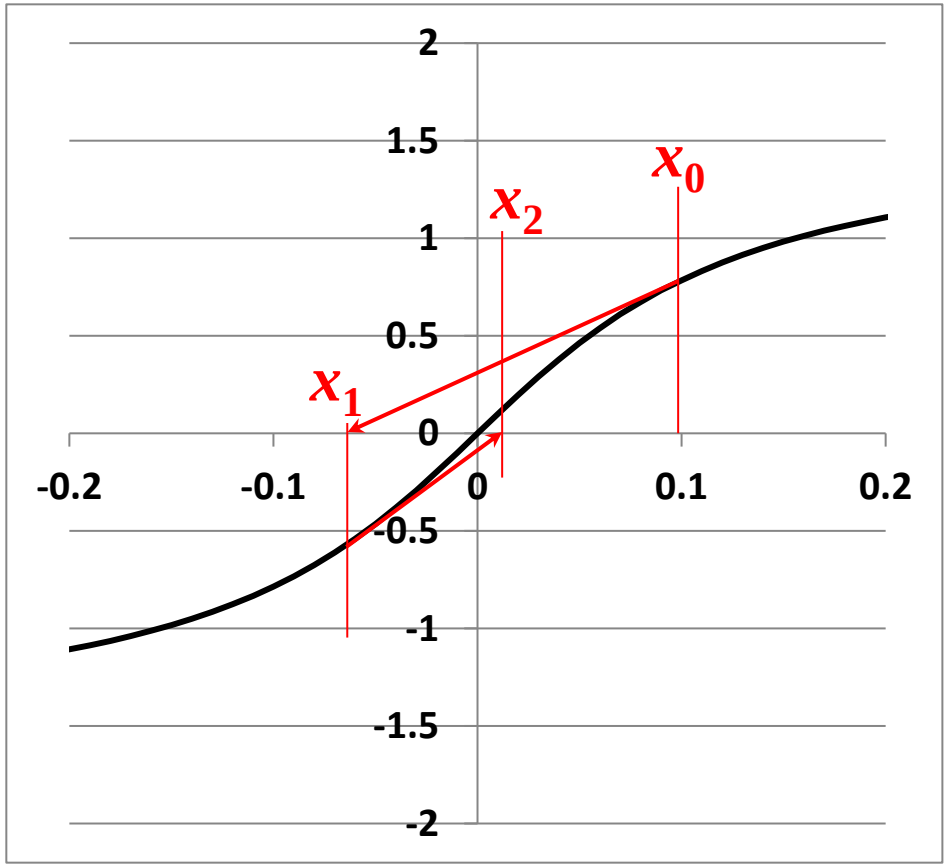
$f(x) = \tan^{-1}(10x)$

initial $x = 0.1$



A case to reach convergence

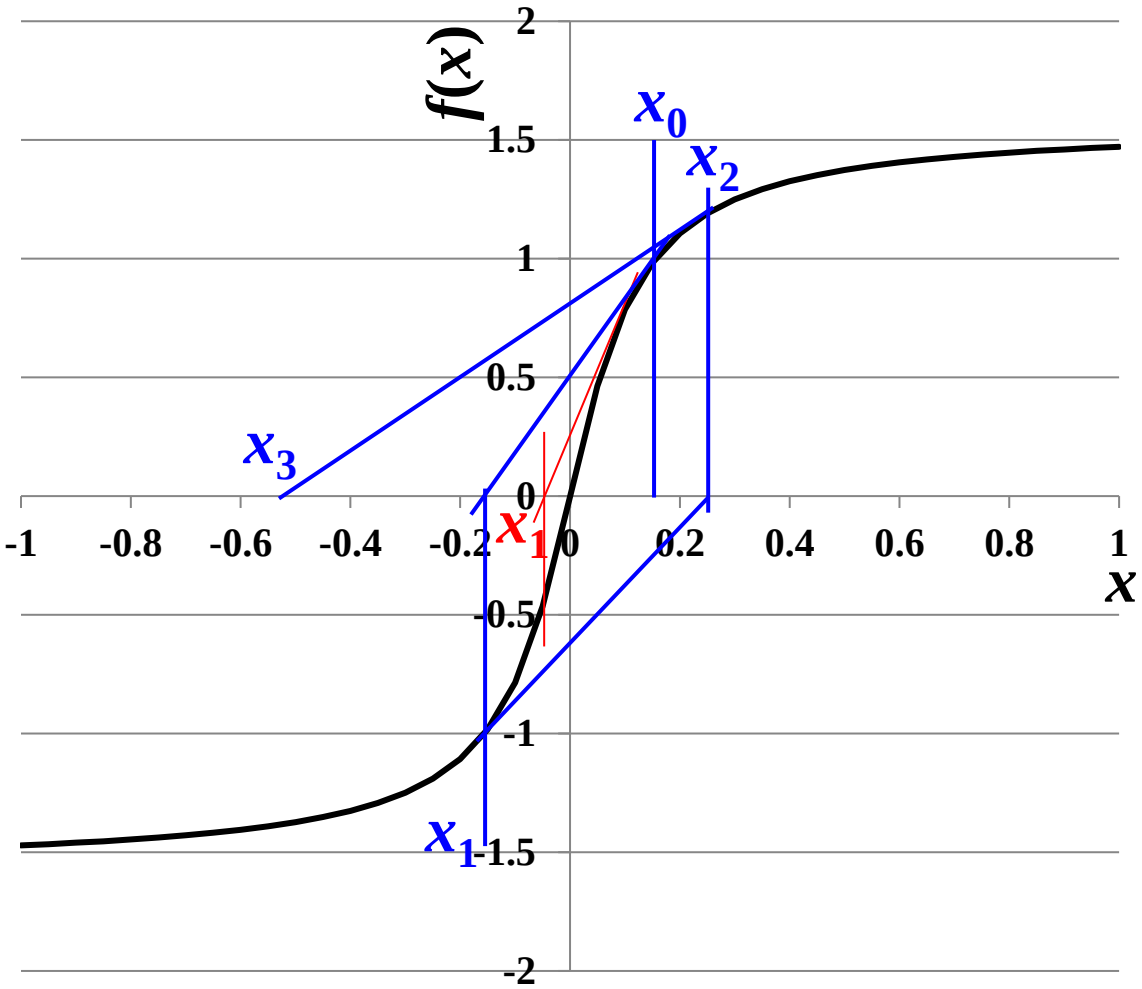
i	x	f(x)	df/dx	dx
0	0.1	0.7854	5	−0.1571
1	−0.05708	−0.5187	7.54257	0.06877
2	0.011686	0.11633	9.86527	−0.0118
3	−0.00011	−0.0011	9.99999	0.00011
4	1.15E−10	1.2E−09	10	−1E−10



Case Newton method fails

$f(x) = \tan^{-1}(10x)$

initial $x = 0.15$



Diverged ($\lambda = 0$)

i	x	f(x)	df/dx	dx
0	0.15	0.98279	3.07692	−0.3194
1	−0.16941	−1.0375	2.58404	0.40152
2	0.232112	1.164	1.56553	−0.7435
3	−0.51141	−1.3777	0.36827	3.74095
4	3.229546	1.53984	0.00958	−160.76
5	−157.529	−1.5702	4E−06	389644
6	389486.7	1.5708	1.1E−12	−1E+12

$$x_{k+1} = x_k - f(x_k) / (f'(x_k) + \lambda)$$

λ: Dumping Factor

Stabilize convergence by choosing λ($\lambda = 1$)

i	x	f(x)	df/dx	dx
0	0.15	0.98279	3.07692	−0.2411
1	−0.09106	−0.7387	5.46675	0.11422
2	0.023161	0.2276	9.49088	−0.0217
3	0.001466	0.01466	9.99785	−0.0013
4	0.000133	0.00133	9.99998	−0.0001
5	1.21E−05	0.00012	10	−1E−05
6	1.1E−06	1.1E−05	10	−1E−06
7	1E−07	1E−06	10	−9E−08
8	9.09E−09	9.1E−08	10	−8E−09
9	8.27E−10	8.3E−09	10	−8E−10

Program: Calculate electron density n_e from E_F in metal

Issues for integrating $N(e)f(e)$

- Wide integration range $E = 0 \sim E_F + \alpha k_B T$ – several eV (accuracy at the order of exp(-α))
- Important range for accuracy is the range of $\alpha k_B T \sim 0.1$ eV around E_F
- For numerical integration, E mesh ΔE should be very small around E_F (if $0.01\alpha k_B T$, ΔE ~1 meV)
  => Not good to use the same ΔE for the whole integration range $E = 0 \sim E_F + \alpha k_B T$

=> - **Divide integration range** (Analytical integration may be employed for $0 \sim E_F - \alpha k_B T$)
- **Better to employ accuracy-guaranteed library for integration**
  python integrate.quad() can accept accuracy as epsrel variable

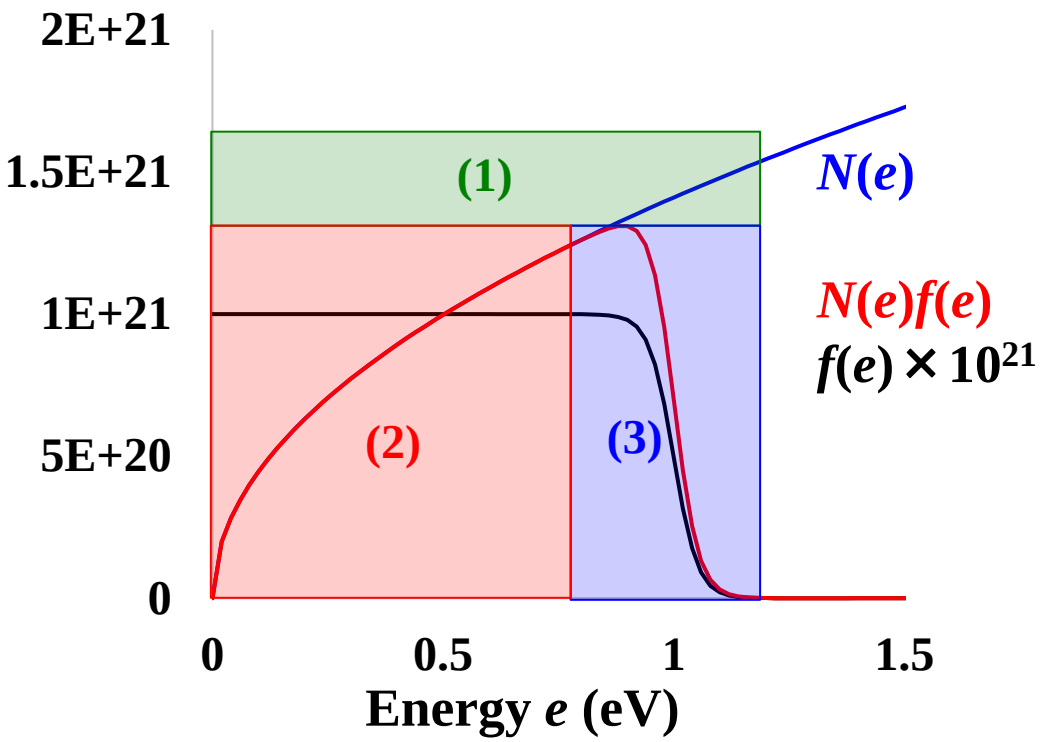
Program: N-integration-metal.py

Ex.: python N-integration-metal.py 300 5.0
At 300 K, E_F = 5.0 eV
Time is measured for 300 cycles calculation

8 digit accuracy (epsrel = 1e-8), α = 6:

range	time (300 cycles)
(1) $0 \sim E_F + \alpha k_B T$	0.109 s
(2) $0 \sim E_F - \alpha k_B T$	0.063 s
(3) $E_F - \alpha k_B T \sim E_F + \alpha k_B T$	0.016 s

(2) + (3) is faster by ~30 % than (1).
Employing analytical integration for (2) is faster by a factor of 10



Program: T dependence of E_F from n_e for metal

$E_F(T)$ is determined by $N_e = \int N(e)f(e,E_F)de$ for the given electron number N_e

$N(e)f(e, E_F)$ is integrated in the range $E = 0 - \infty$ (acutualy up to $E_F + \alpha k_B T$)

The initial value of $E_F(T)$ can be taken as the analytical form of $E_F(0)$ at 0 K.

Since the variation of $E_F(T)$ is small, the Newton method stability converges.

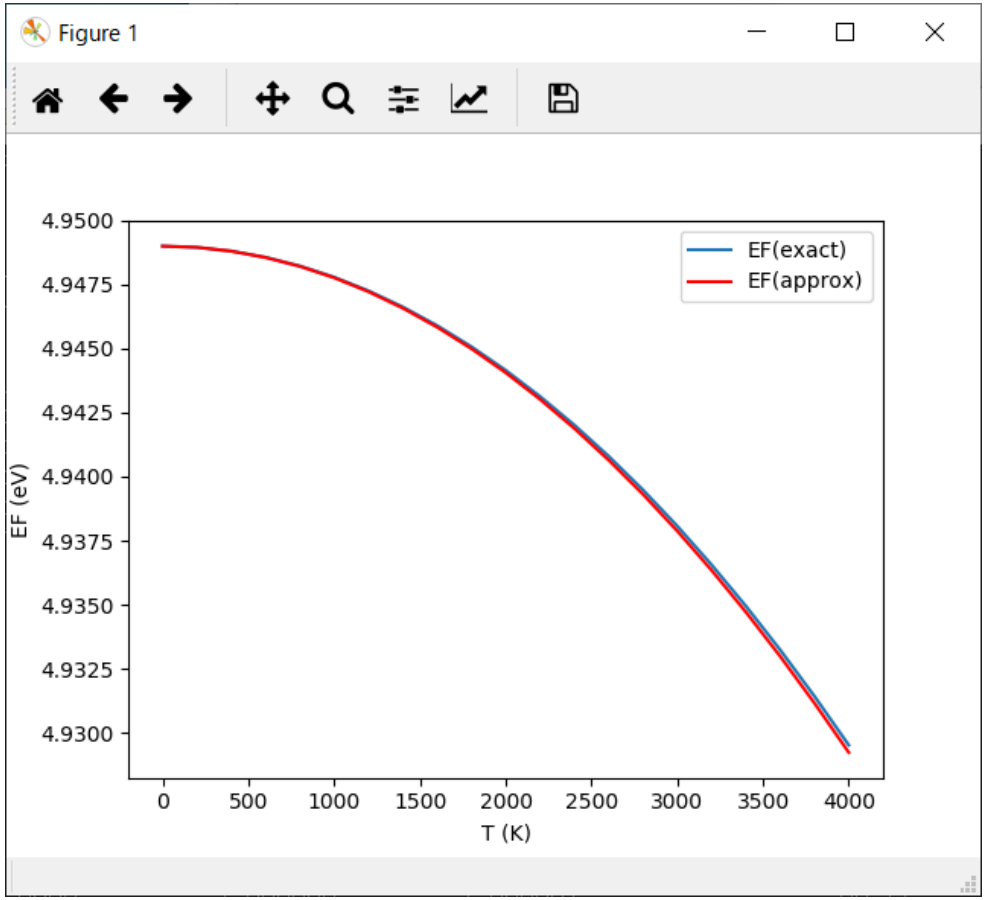
Compare with the approx. form $E_F(T) = EF(0) - \frac{\pi^2}{6}(k_B T)^2 N'(E_F(0))/N(E_F(0))$

Program: EF-T-metal.py

Ex.: python EF-T-metal.py

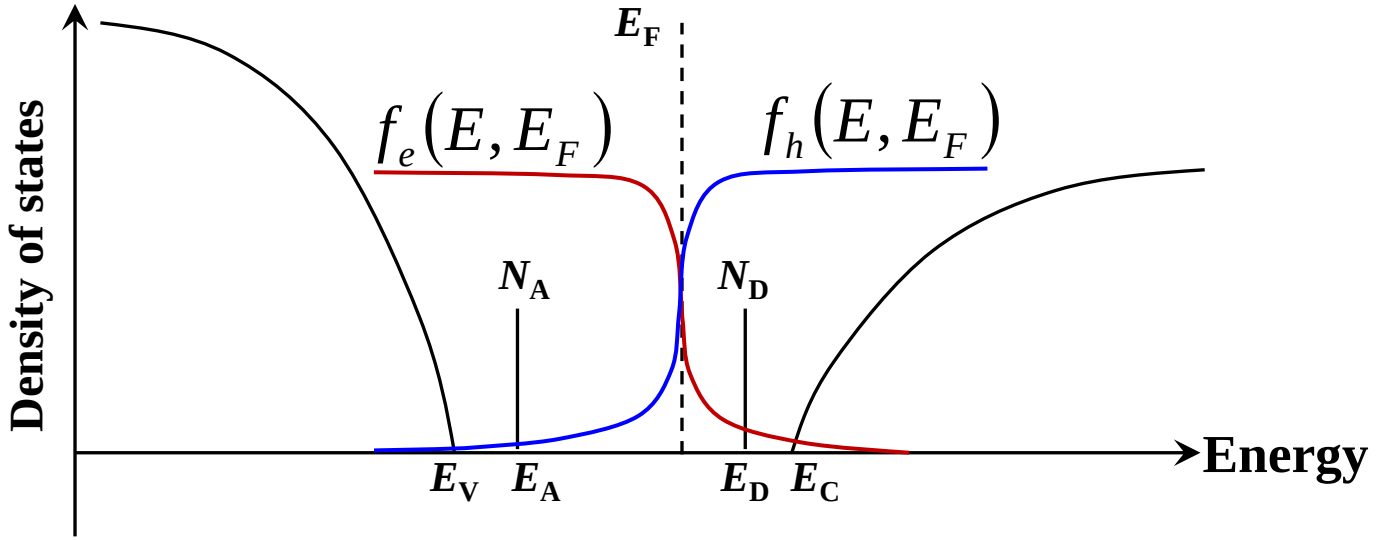
For $n_e = 5x10_{22}$ cm^{-3}

T (K)	E_F (Newton, eV)	E_F (approx., eV)
0	4.948988	4.948988
600	4.948554	4.948544
1200	4.947248	4.947211
1800	4.945069	4.944990
2400	4.942013	4.941880
3000	4.938075	4.937882
3600	4.933247	4.932994
4000	4.929529	4.929243



Density of states, n_e, and n_h in semiconductor

Total density of states: $\boldsymbol{D(E) = D_e(E) + D_h(E) + D_D(E) + D_A(E)}$



Valence band

$D_h(E) = D_{V0}\sqrt{E_V - E}$

$D_A(E) = N_A\delta(E - E_A)$

$f_h(E, E_F) = \frac{1}{\exp(\beta(E_F - E))+1}$

Free hole density

$n_h = \int_{-\infty}^{E_V} f_h(E, E_F) D_h(E) dE$

Ionized acceptor density

$N_A^- = N_A(1 - f_h(E_A, E_F))$

Conduction band

$D_e(E) = D_{C0}\sqrt{E - E_C}$

$D_D(E) = N_D\delta(E - E_D)$

$f_e(E, E_F) = \frac{1}{\exp(\beta(E - E_F))+1}$

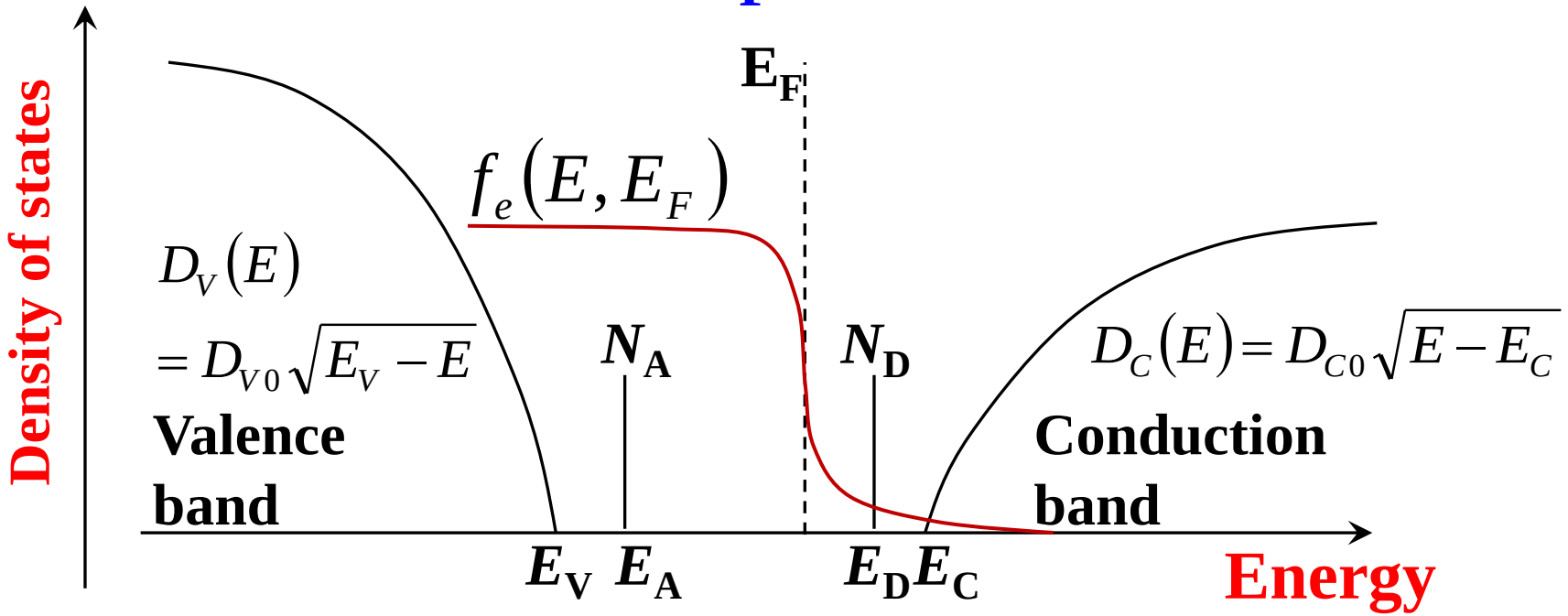
Free electron density

$n_e = \int_{E_C}^{\infty} f_e(E) D_e(E) dE$

Ionized donor density

$N_D^+ = N_D(1 - f_e(E_D, E_F))$

How to determine E_F for semiconductors



$$E_g = E_C - E_V$$

Charge neutrality condition

$$N_A^- + N_e = N_D^+ + N_h \quad \Rightarrow \quad E_F$$

$$N_e = \int_{E_C}^{\infty} D_C(E) f_e(E, E_F) dE$$

$$N_D^+ = N_D[1 - f_e(E_D, E_F)]$$

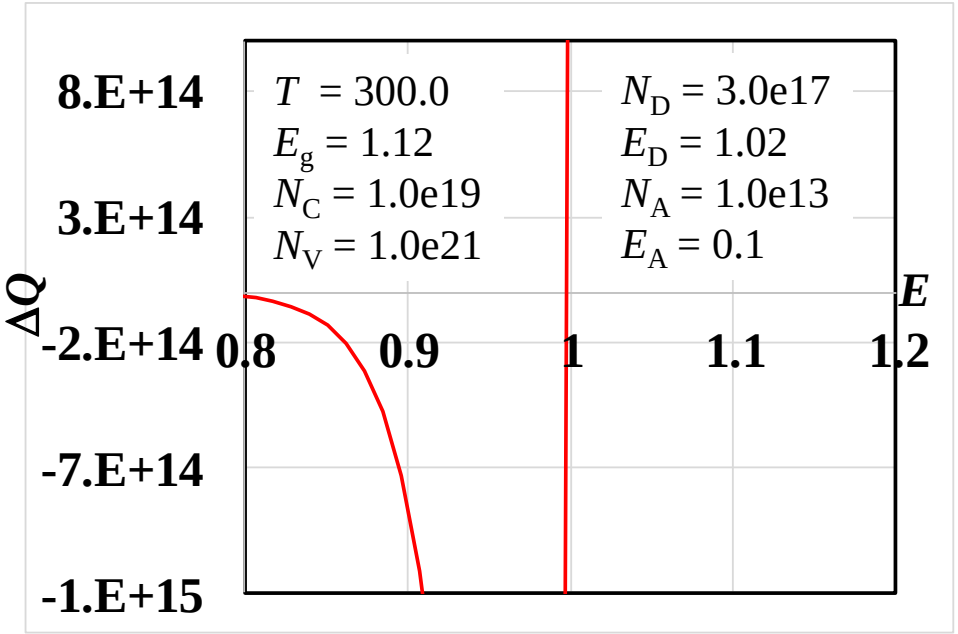
How to calculate E_F: Illustrative solution

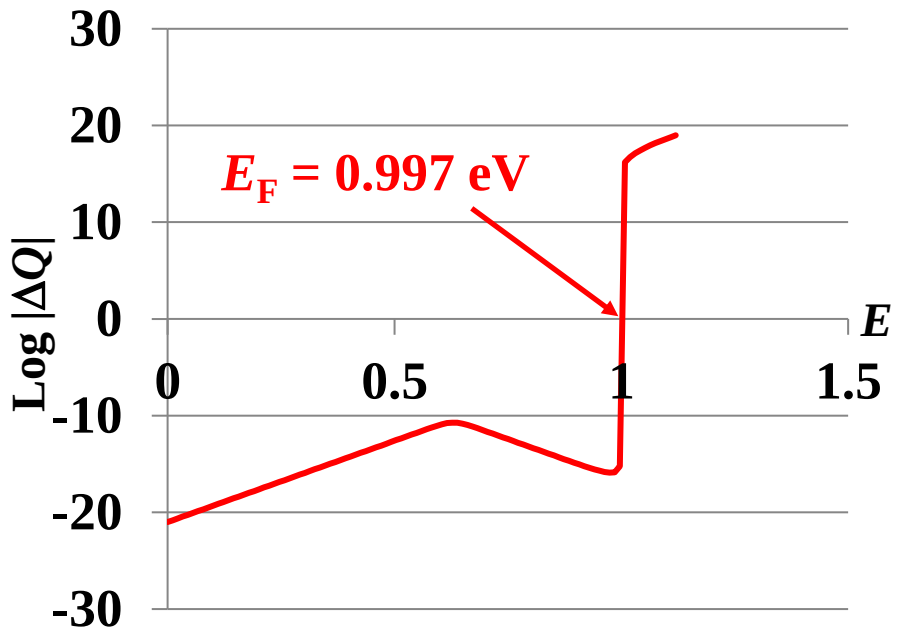
$$N_e = \int_{E_C}^{\infty} D_C(E) f_e(E, E_F) dE \qquad N_h = \int_{E_C}^{\infty} D_V(E) f_h(E, E_F) dE$$

$$N_D^+ = N_D[1 - f_e(E_D, E_F)] \qquad N_A^- = N_A[1 - f_h(E_A, E_F)]$$

$$f_h(E, E_F) = 1 - f_e(E, E_F)$$

Plot $\Delta Q = (N_A^- + N_e) - (N_D^+ + N_h)$ w.r.t. E_F and find $\Delta Q = 0$





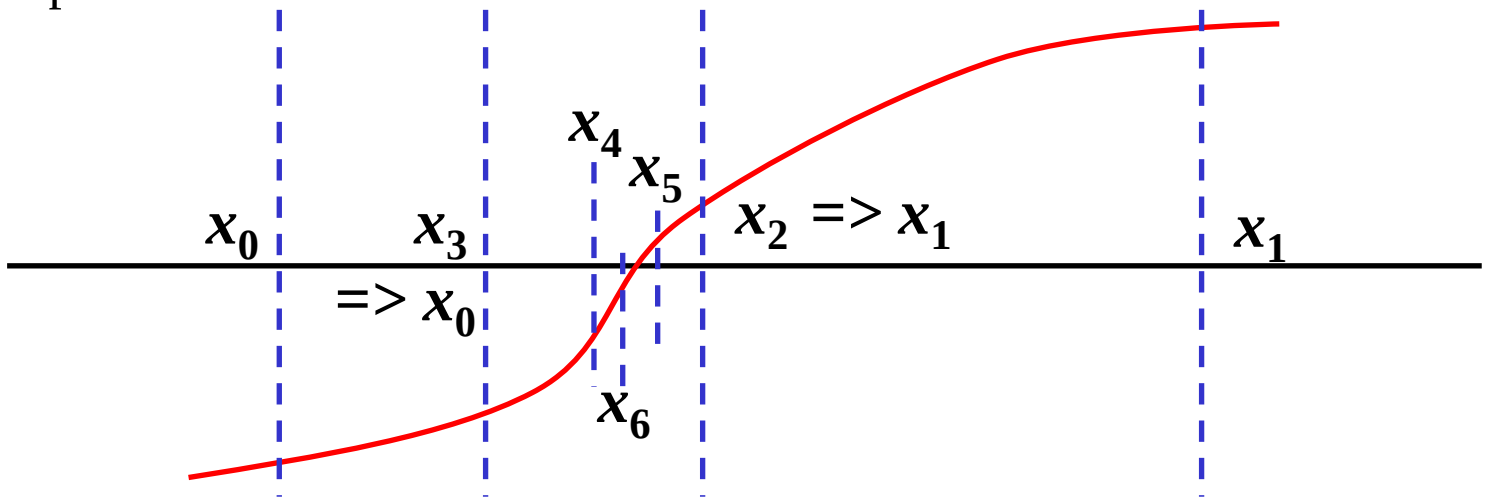
Bisection method (二分法): Continuous func（連続関数)

Solution of $f(x) = 0$ for (monotonic) continuous function $f(x)$

1. **Start from a range $[x_0, x_1]$ where $f(x_0) < 0$ & $f(x_1) > 0$**
   (or $f(x_0) > 0$ & $f(x_1) < 0$)
   *** Solution exist in this range for a monotonic function**
2. **Solve the equation by the following iterative procedure**

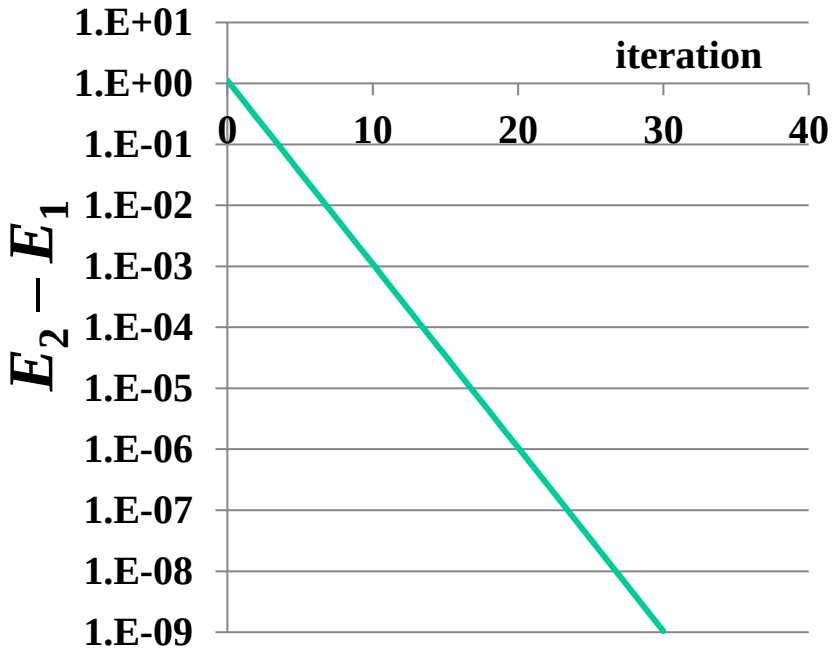
Case $f(x_0) < 0$ and $f(x_1) > 0$: Judge by $f(x_0) \cdot f(x_1) < 0$

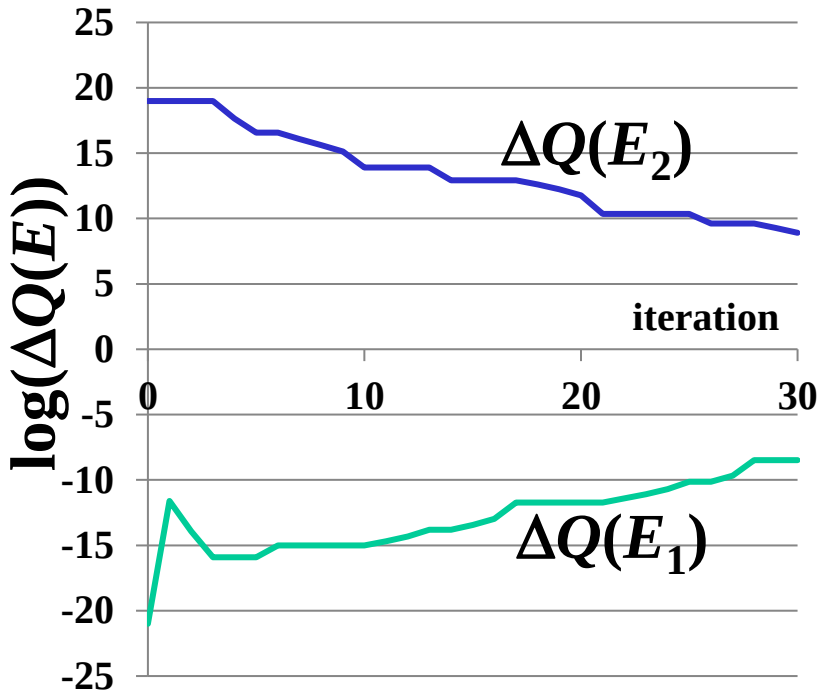
1. $x_2 = (x_0 + x_1) / 2.0$
2. If $f(x_2) > 0$ ($f(x_0) \cdot f(x_2) < 0$), x_1 is replaced with x_2
   If $f(x_2) < 0$ ($f(x_1) \cdot f(x_2) < 0$), x_0 is replaced with x_2
3. Solution x_2 is obtained when $|x_1 - x_0|$, $|f(x_1) - f(x_0)|$ becomes less than EPS.
4. Repeat 1 – 3



E_F by bisection method: Convergence procedure

Initial range: $[E_1, E_2] = [E_V = 0, E_C = E_g]$
Find $\Delta Q = (N_A^- + N_e) - (N_D^+ + N_h) = 0$





After 30 times iterations

E_F = [0.9985173589, 0.9985173599]

dQ = [-3×10^8, 8×10^8]

Program: EF-T-semiconductor.py

Program: EF-T-semiconductor.py

Usage: **python EF-T-semiconductor.py EA NA ED ND Ec Nv Nc**

Ex.: **python EF-T-semiconductor.py 0.05 1.0e15 0.95 1.0e16 1.0 1.2e19 2.1e18**

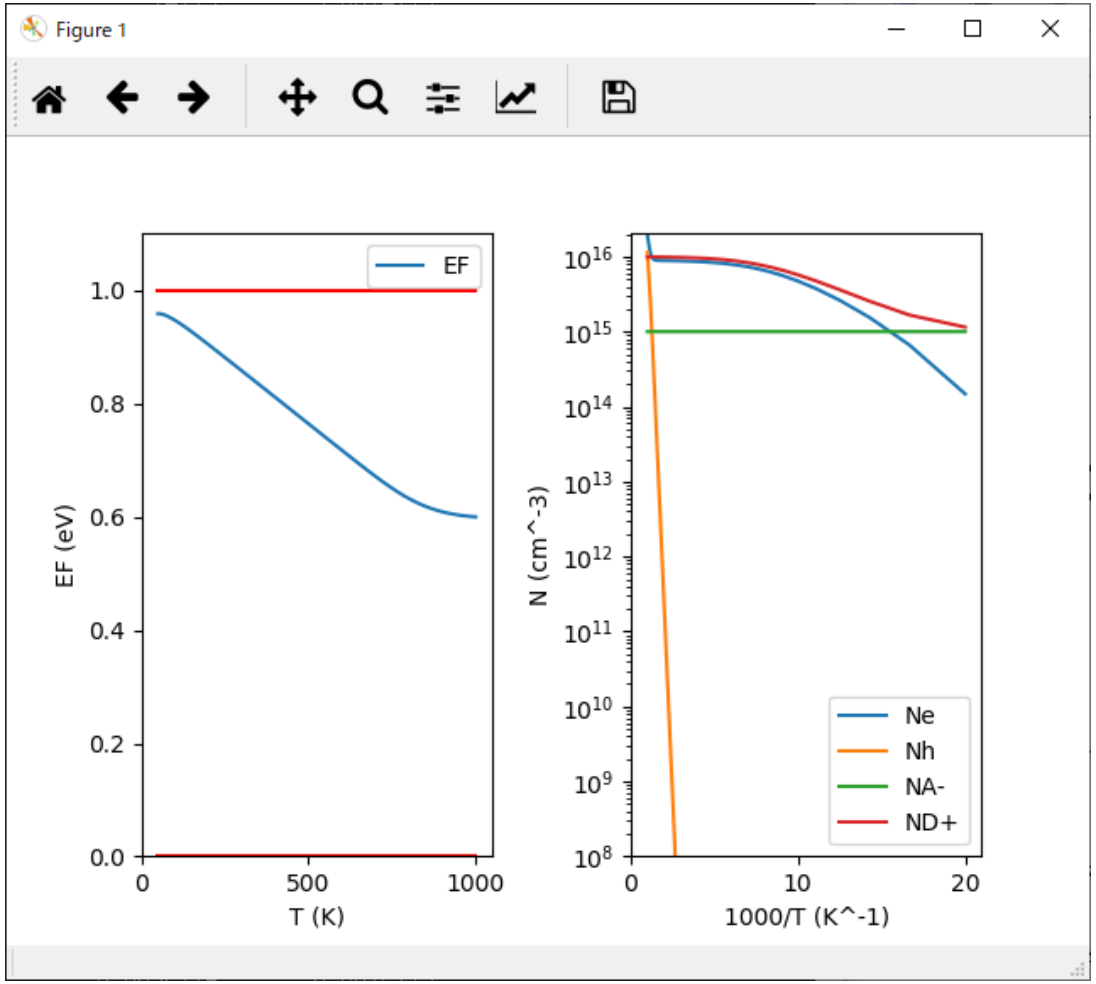
$E_c = 0$, $E_c = 1.0$ eV (= band gap)

$E_A = 0.05$ eV, $N_A = 10^{15}$ cm^{-3}

$E_D = 0.95$ eV, $N_D = 10^{16}$ cm^{-3}

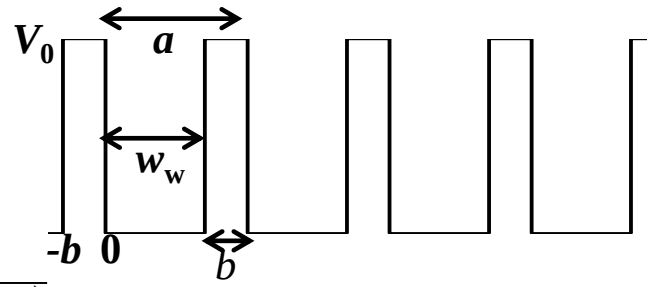
$N_c = 1.2 \times 10^{19}$ cm^{-3}

$N_v = 2.1 \times 10^{18}$ cm^{-3}



Multi-values equation: Kronig-Penney model

Solution of $\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V(x)\right)\phi = E\phi$



$\boldsymbol{\phi_k(x) = \exp(ikx)u(x),\ u(x+a) = u(x)}$

In well: $\phi(x) = A\exp(i\alpha x) + B\exp(-i\alpha x)$ $\quad \alpha = \sqrt{2mE}/\hbar$

In barrier: $\phi(x) = C\exp(\beta x) + D\exp(-\beta x)$ $\quad \beta = \sqrt{2m(V_0 - E)}/\hbar$

Boundary condition: $\boldsymbol{\phi_k(x)}$ and $\boldsymbol{\phi_k'(x)}$ are continuous at $x = 0$ and $-b$

Bloch's theorem : $\boldsymbol{\phi_k(x+a) = \lambda\phi_k(x),\ \lambda = \exp(ika)}$

$$\begin{pmatrix} 1 & 1 & -1 & -1 \\ i\alpha & -i\alpha & -\beta & \beta \\ \exp(i\alpha w_w) & \exp(-i\alpha w_w) & -\lambda\exp(-\beta b) & -\lambda\exp(\beta b) \\ i\alpha\exp(i\alpha w_w) & -i\alpha\exp(-i\alpha w_w) & -\beta\lambda\exp(-\beta b) & \beta\lambda\exp(\beta b) \end{pmatrix}\begin{pmatrix} A \\ B \\ C \\ D \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}$$

The determinant of the left matrix must be 0:

$$\boldsymbol{\cos ka = \left(\frac{\beta(E)^2 - \alpha(E)^2}{2\alpha(E)\beta(E)}\sin\alpha(E)w_w \sinh\beta(E)b + \cos\alpha(E)w_w\cosh\beta(E)b\right)}$$

Scan *E* in possible range to find all the solutions,
then use them for initial values
to obtain accurate values by Newton-Raphson method

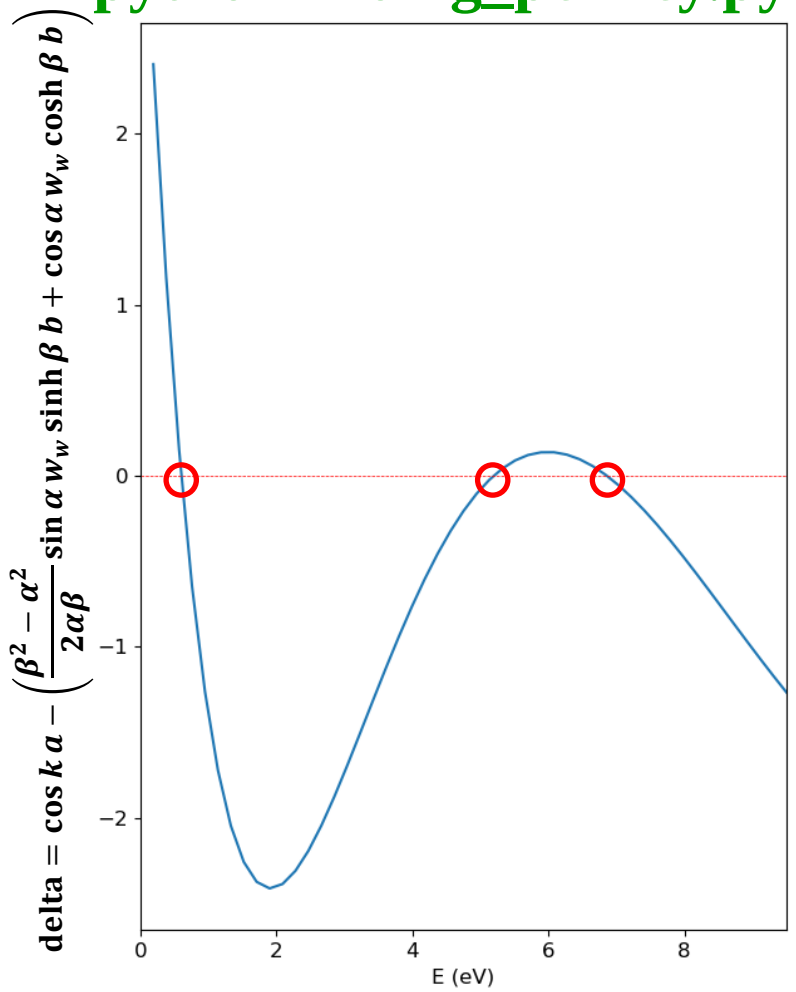
Program: Kronig-Penney model

Program: kronig_penney.py

Lattice parameter (Si) a = 5.4064 Å Effective mass m* = $1.0m_e$

Barrier width 0.5 Å Barrier height 10.0 eV

python kronig_penney.py



python kronig_penney.py band