Physical Chemistry 2

Lecture 5. Other problems in one dimension

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paradichlorobenzene1724@gmail.com
kadryjh1724@snu.ac.kr

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서울대학교
SEOUL NATIONAL UNIVERSITY
Department of Chemistry

Jiho Son

Topics in Lecture 5

Derivation of uncertainty principle

3D particle-in-a-box problem

Step potential

Electron tunneling

In Atkins' *Physical Chemistry* (11th ed.),

7D Translational motion

Main Reference for this lecture

David J. Griffiths, Darrell F. Schroeter
Introduction to Quantum Mechanics (3rd ed.), Cambridge University Press (2018).

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Uncertainty principle

Consider arbitrary observable A and B. Then variation of them are given by

$$\sigma_A^2 = \left\langle (\hat{A} - \langle A \rangle)^2 \right\rangle = \left\langle (\hat{A} - \langle A \rangle)\Psi \,|\, (\hat{A} - \langle A \rangle)\Psi \right\rangle \equiv \langle f \,|\, f \rangle$$

Similarly, define g:

$$\sigma_B^2 = \left\langle (\hat{B} - \langle B \rangle)^2 \right\rangle = \left\langle (\hat{B} - \langle B \rangle)\Psi \,|\, (\hat{B} - \langle B \rangle)\Psi \right\rangle \equiv \langle g \,|\, g \rangle$$

From *Cauchy-Schwarz inequality*, we yield

$$\sigma_A^2 \sigma_B^2 = \langle f \,|\, f \rangle \langle g \,|\, g \rangle \geq |\langle f \,|\, g \rangle|^2$$

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Uncertainty principle

Let's get help from the next equation. For arbitrary complex number z, the following holds:

$$|z|^2 = [\Re(z)]^2 + [\Im(z)]^2 \geq [\Im(z)]^2 = \left[\frac{1}{2i}(z - z^*)\right]^2$$

Then

$$\sigma_A^2\sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2 \geq \left(\frac{1}{2i}[\langle f | g \rangle - \langle g | f \rangle]\right)^2$$

$$\langle f | g \rangle = \left\langle (\hat{A} - \langle A \rangle)\Psi \,|\, (\hat{B} - \langle B \rangle)\Psi \right\rangle = \left\langle \Psi \,|\, (\hat{A} - \langle A \rangle)(\hat{B} - \langle B \rangle) \,|\, \Psi \right\rangle = \left\langle \hat{A}\hat{B} \right\rangle - \left\langle \hat{A} \right\rangle \left\langle \hat{B} \right\rangle$$

$$\langle g | f \rangle = \left\langle \hat{B}\hat{A} \right\rangle - \left\langle \hat{B} \right\rangle \left\langle \hat{A} \right\rangle$$

Therefore

$$\langle f | g \rangle - \langle g | f \rangle = \left\langle \hat{A}\hat{B} \right\rangle - \left\langle \hat{B}\hat{A} \right\rangle = \left\langle \left[\hat{A}, \hat{B}\right] \right\rangle, \qquad \therefore\ \sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\left\langle \left[\hat{A}, \hat{B}\right] \right\rangle\right)^2$$

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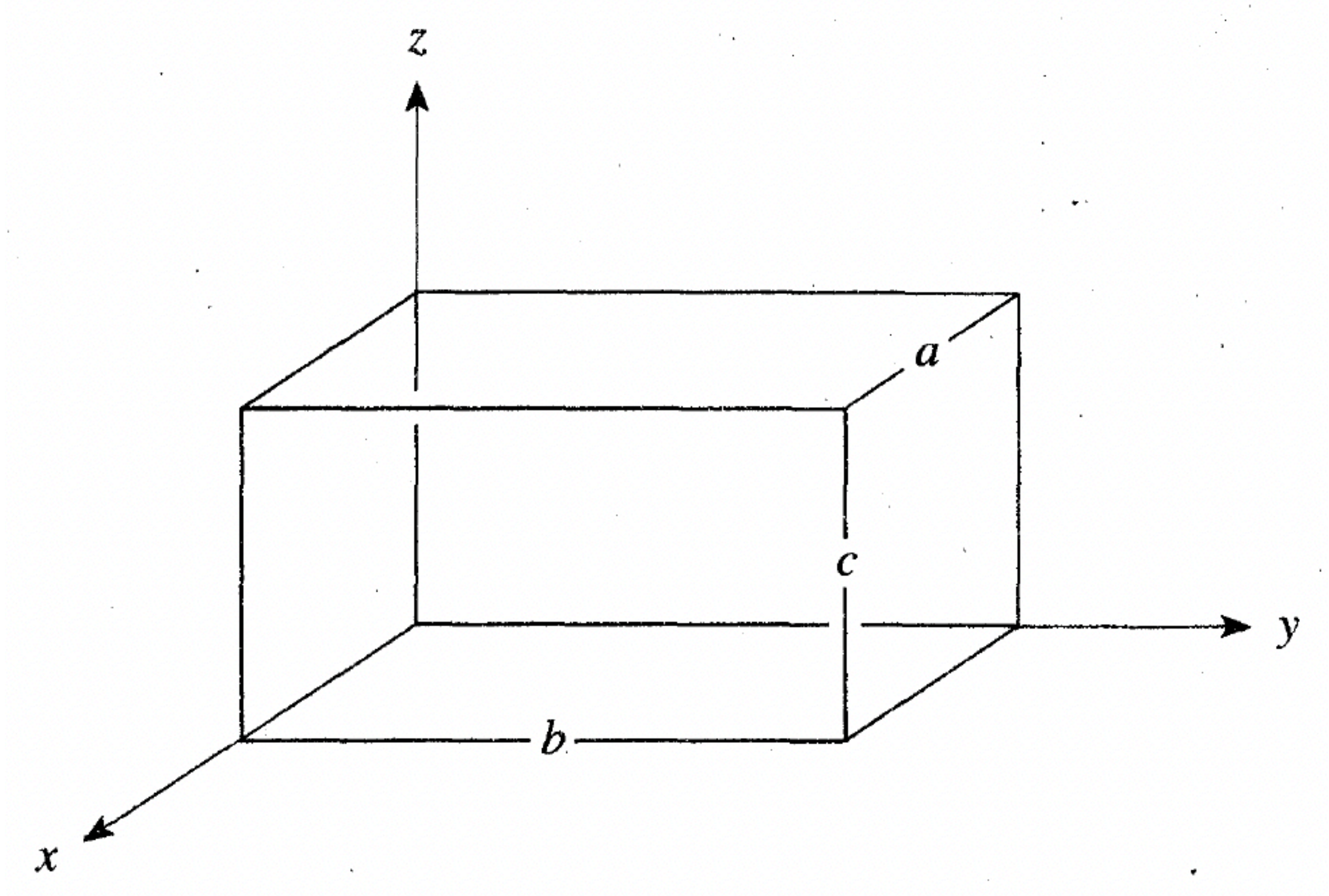
3D particle in a box

Hamiltonian becomes three-dimensional. $-\frac{\hbar^2}{2m}\nabla^2\psi(x,y,z) = E\psi(x,y,z)$

Potential energy is zero inside the box, but infinity otherwise.

$$V(x,y,z) = 0 \text{ if } 0 \leq x,y,z \leq a,b,c, \quad V(x,y,z) = \infty \text{ otherwise}$$



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3D particle in a box

Separation of variables. Separate each directions! $\psi(x, y, z) = X(x)Y(y)Z(z)$

$$-\frac{\hbar^2}{2m}\left(YZ\frac{d^2X}{dx^2} + ZX\frac{d^2Y}{dy^2} + XY\frac{d^2Z}{dz^2}\right) = EXYZ$$

Divide with *XYZ* and separate the energy: $E = E_x + E_y + E_z$. Then we yield 3 identical equations.

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_xX, \quad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_yY, \quad -\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} = E_zZ$$

Therefore the solution of 3D particle in a box is straightforward.

$$\psi(x, y, z) = X(x)Y(y)Z(z) = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x\pi x}{a} \sin\frac{n_y\pi y}{b} \sin\frac{n_z\pi z}{c} \quad (n_x, n_y, n_z = 1,2,\ldots)$$

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \quad (n_x, n_y, n_z = 1,2,\ldots)$$

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3D particle in a box

Degeneracy. For convenience, assume *a*=*b*=*c*. Then, energy levels are

$$E = E_x + E_y + E_z = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \quad (n_x, n_y, n_z = 1,2,\ldots)$$

The ground state is

$$E_{111} = \frac{3h^2}{8ma^2}$$

But we have three degenerate excited states. We call this phenomenon as degeneracy.

$$E_{112} = E_{121} = E_{211} = \frac{6h^2}{8ma^2}$$

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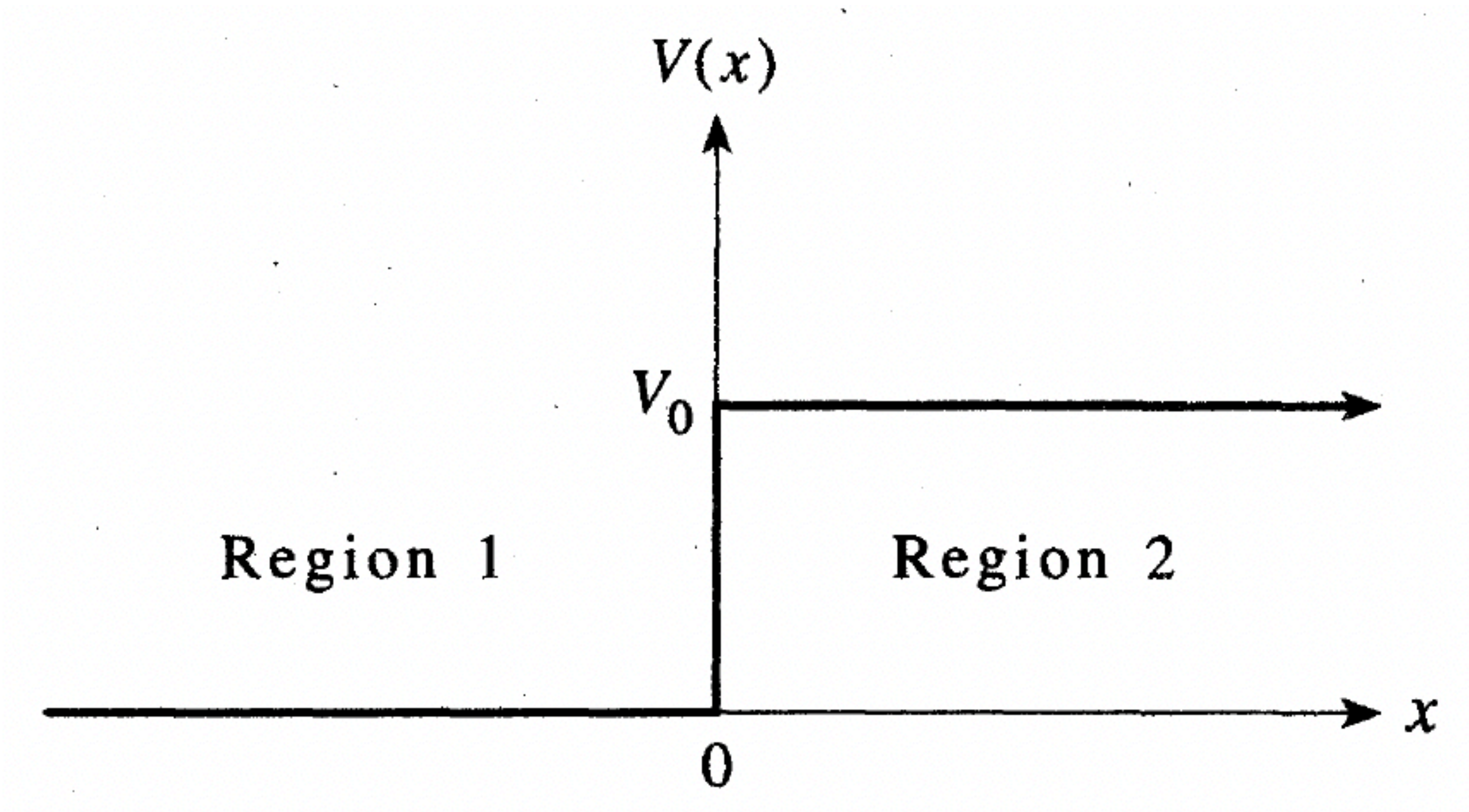
Problems in 1 dimension

Step potential.



What should we use? *Boundary conditions on x=0*.
- Continuity of wavefunction
- Continuity of first derivative of wavefunction.

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Step potential

Problem 9. Scattering on step function

(a) Let $\psi_1(x)$ denote the wavefunction for $x < 0$ and $\psi_2(x)$ for $x > 0$. Then we can set

$$\psi_1(x) = Ae^{ik_0x} + Be^{-ik_0x}, \ \psi_2(x) = Ce^{ikx} \qquad \left(k_0^2 = \frac{2mE}{\hbar^2}, \ k^2 = \frac{2m(E-V_0)}{\hbar^2}\right)$$

since $E > V_0$. Boundary conditions are

$$\psi_1(0) = \psi_2(0) \Longrightarrow A + B = C$$

$$\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0} \Longrightarrow ik_0A - ik_0B = ikC$$

(b) Since $A + B = C$ and $A - B = \frac{k}{k_0}C$, we can obtain

$$\frac{C}{A} = \frac{2k_0}{k_0+k}, \ \frac{B}{A} = \frac{C}{A}\frac{B}{C} = \frac{2k_0}{k_0+k} \cdot \frac{k_0-k}{2k_0} = \frac{k_0-k}{k_0+k}$$

Therefore reflection and transmission coefficients are

$$R = \left|\frac{B}{A}\right|^2 = \frac{(k_0-k)^2}{(k_0+k)^2}, \ T = \frac{k}{k_0}\left|\frac{C}{A}\right|^2 = \frac{4kk_0}{(k_0+k)^2}$$

- When $E \to V_0$, $k \to 0$. Therefore $T \to 0$ and $R \to 1$.
- When $E \to \infty$, $k \to k_0$. Therefore $T \to 1$ and $R \to 0$.

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(c) Let $\psi_1(x)$ denote the wavefunction for $x<0$ and $\psi_2(x)$ for $x>0$. Then we can set

$$\psi_1(x) = Ae^{ik_0x} + Be^{-ik_0x},\ \psi_2(x) = Ce^{-\kappa x} \qquad (k_0^2 = \frac{2mE}{\hbar^2},\ \kappa^2 = \frac{2m(V_0-E)}{\hbar^2})$$

since $0<E<V_0$. Boundary conditions are

$$\psi_1(0) = \psi_2(0) \implies A+B=C$$
$$\left.\frac{d\psi_1}{dx}\right|_{x=0} = \left.\frac{d\psi_2}{dx}\right|_{x=0} \implies ik_0A - ik_0B = -\kappa C$$

(d) From the boundary condition, we can get

$$\frac{C}{A} = \frac{2}{1+ik/k_0},\ \frac{B}{A} = \frac{C}{A}\cdot\frac{B}{C} = \frac{2}{1+ik/k_0}\frac{1-ik/k_0}{2} \implies R = \left|\frac{B}{A}\right|^2 = 1$$

Therefore, $T=0$ indeed. We can justify this result by calculating the probability current. Since

$$\vec{j} = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*) = \frac{\hbar}{2mi}|C|^2(e^{-\kappa x}\partial_x e^{-\kappa x} - e^{-\kappa x}\partial_x e^{-\kappa x}) = 0$$

we can justify the result $T=0$, since there is no probability current in $x>0$.

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Problems in 1 dimension

Electron tunneling. Consider the scattering problem for the finite square well potential given by

$$V(x) = +V_0 \ \ (|x| \le a), \quad 0 \ \ (\mathrm{o.w.})$$

where V_0 is a positive constant.

(a) Region 1 : $x < -a$, Region 2 : $|x| < a$, Region 3 : $x > a$. Then

$$\psi_1(x) = Ae^{ikx} + Be^{-ikx}, \ \psi_2(x) = Ce^{\kappa x} + De^{-\kappa x}, \ \psi_3(x) = Fe^{ikx}$$

where $k^2 = \dfrac{2mE}{\hbar^2}$, $\kappa^2 = \dfrac{2m(V_0 - E)}{\hbar^2}$, $T = \left|\dfrac{F}{A}\right|^2$. Boundary conditions are

$$\psi_1(-a) = \psi_2(-a) \implies Ae^{-ika} + Be^{ika} = Ce^{-\kappa a} + De^{\kappa a} \tag{1}$$

$$\left.\frac{d\psi_1}{dx}\right|_{-a} = \left.\frac{d\psi_2}{dx}\right|_{-a} \implies ikAe^{-ika} - ikBe^{ika} = \kappa Ce^{-\kappa a} - \kappa De^{\kappa a} \tag{2}$$

$$\psi_2(a) = \psi_3(a) \implies Ce^{\kappa a} + De^{-\kappa a} = Fe^{ika} \tag{3}$$

$$\left.\frac{d\psi_2}{dx}\right|_{a} = \left.\frac{d\psi_3}{dx}\right|_{a} \implies \kappa Ce^{\kappa a} - \kappa De^{-\kappa a} = ikFe^{ika} \tag{4}$$

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By adding and subtracting equations (3) and (4)/ik, we get

$$C = \frac{e^{ika}e^{-\kappa a}}{2}\left(1 + i\frac{k}{\kappa}\right)F,\ D = \frac{e^{ika}e^{\kappa a}}{2}\left(1 - i\frac{k}{\kappa}\right)F$$

By equations (1) and (2),

$$2Ae^{-ika} = \left(1 - i\frac{\kappa}{k}\right)Ce^{-\kappa a} + \left(1 + \frac{\kappa}{k}\right)De^{\kappa a}$$

By substituting C and D, we get

$$\begin{aligned}\frac{A}{F}\cdot 4e^{-2ika} &= \left(2 + i\frac{k}{\kappa} - i\frac{\kappa}{k}\right)e^{-2\kappa a} + \left(2 + i\frac{\kappa}{k} - i\frac{k}{\kappa}\right)e^{-2\kappa a} \\ &= 4\cosh(2\kappa a) + 2i\frac{\kappa^2 - k^2}{\kappa k}\sinh(2\kappa a)\end{aligned}$$

Since $T^{-1} = \left|\frac{A}{F}\right|^2$,

$$16\left|\frac{A}{F}\right|^2 = 16\cosh^2(2\kappa a) + 4\frac{(\kappa^2 - k^2)^2}{\kappa^2 k^2}\sinh^2(2\kappa a) = 16 + 4\frac{(\kappa^2 + k^2)^2}{\kappa^2 k^2}\sinh^2(2\kappa a)$$

From the definition of κ and k, we get

$$\boxed{T^{-1} = 1 + \frac{V_0^2}{4E(V_0 - E)}\sinh^2(2\kappa a)}$$

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(b) For $E = V_0$ case, consider about the $E \to V_0$ ($\kappa \to 0$) limit. Assume $\kappa a << 1$. Then,

$$\sinh(2\kappa a) = \frac{e^{2\kappa a} - e^{-2\kappa a}}{2} \sim \frac{(1+2\kappa a) - (1-2\kappa a)}{2} = 2\kappa a$$

Therefore

$$T^{-1} \sim 1 + \frac{V_0^2}{4E(V_0 - E)} \cdot 4\kappa^2 a^2 = 1 + \frac{2ma^2V_0^2}{E\hbar^2} \sim \boxed{1 + \frac{2ma^2V_0}{\hbar^2}}$$

For $E > V_0$ case, we can just replace κ with ik'. If we use the identity $\sinh(iz) = i\sin(z)$,

$$T^{-1} = 1 + \frac{((ik')^2 + k^2)^2}{4(ik')^2k^2}\sinh^2(2ik'a) = 1 + \frac{(k^2 - k'^2)^2}{4k'^2k^2}\sin^2(2k'a) = \boxed{1 + \frac{V_0^2}{4E(E - V_0)}\sin^2(2k'a)}$$

(c) From the T value we calculated in (a) and (b),

$$E < V_0 \ : \ T^{-1} = 1 + \frac{\sinh^2(2\kappa a)}{4\epsilon(1-\epsilon)}$$

$$E > V_0 \ : \ T^{-1} = 1 + \frac{\sin^2(2k'a)}{4\epsilon(\epsilon - 1)}$$

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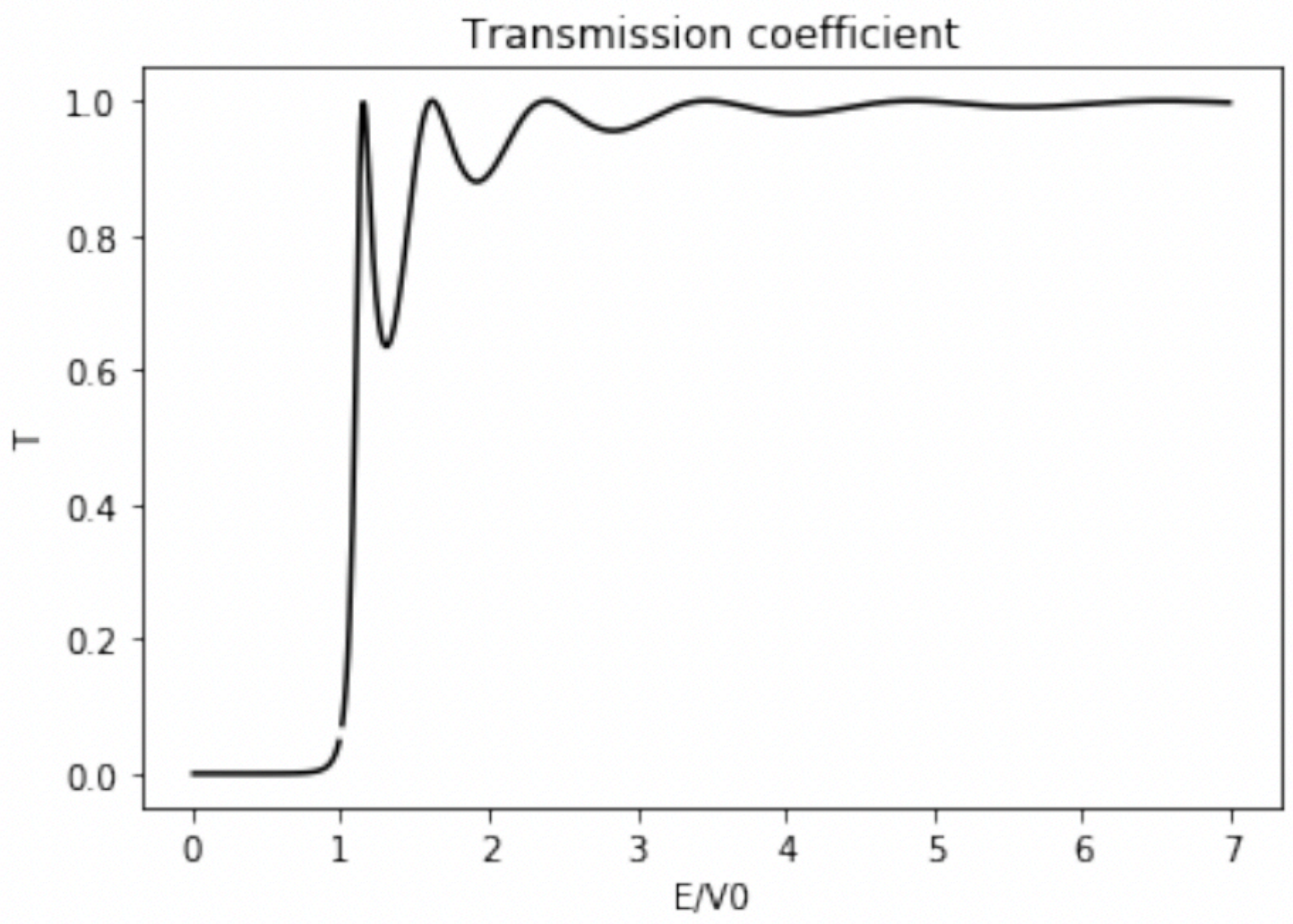
Since $\kappa a = \sqrt{\frac{2ma^2V_0}{\hbar^2}(1-\epsilon)} = R\sqrt{1-\epsilon}$ and $k'a = R\sqrt{\epsilon - 1}$

$$E < V_0 \;:\; T^{-1} = 1 + \frac{\sinh^2(2R\sqrt{1-\epsilon})}{4\epsilon(1-\epsilon)}$$

$$E > V_0 \;:\; T^{-1} = 1 + \frac{\sin^2(2R\sqrt{\epsilon-1})}{4\epsilon(\epsilon-1)}$$

Source code in the attached file.



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