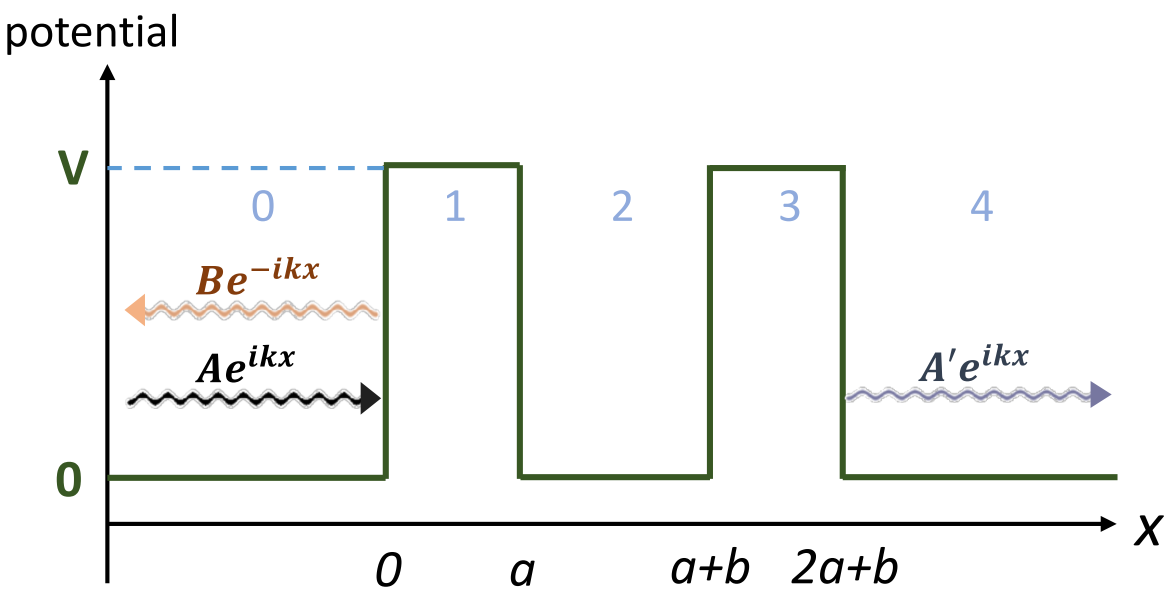
# Problem 1: Multiple barriers

For the following system, use Matlab to:

1. Calculate the coefficients A' of $\psi$ after two finite barriers via transfer matrix approach
2. Calculate transmission probability ($T = \frac{|A'|^2}{|A|^2}$) in case of *E*>*V*

Choose *E* = 4 eV, *V* = 2 eV, *a* = 0.1 nm, *b* = 0.3 nm




$$\psi = \begin{cases} Ae^{ikx} + Be^{-ikx}, x < 0 \\ A'e^{ikx}, x > 2a + b \end{cases}$$

$$\begin{pmatrix} A \\ B \end{pmatrix} = T_{04} \begin{pmatrix} A' \\ B' \end{pmatrix}, \text{where } B' = 0$$

$$k = \sqrt{\frac{2m}{\hbar^2}(E - V)}$$

# Problem 1: Multiple barriers

- Penetration-though-barriers problem can be found in many quantum mechanics textbooks. Here I attached the second chapter from Atkin's book *Molecular Quantum Mechanics* (I think the book is very clear). Section 2.10 is directly relevant to it.

- The transfer matrices can be derived, or you can refer to the scanned pages of Gilmore's book *Elementary Quantum Mechanics in One Dimension* (I've highlighted the most useful parts, in page 13~17)

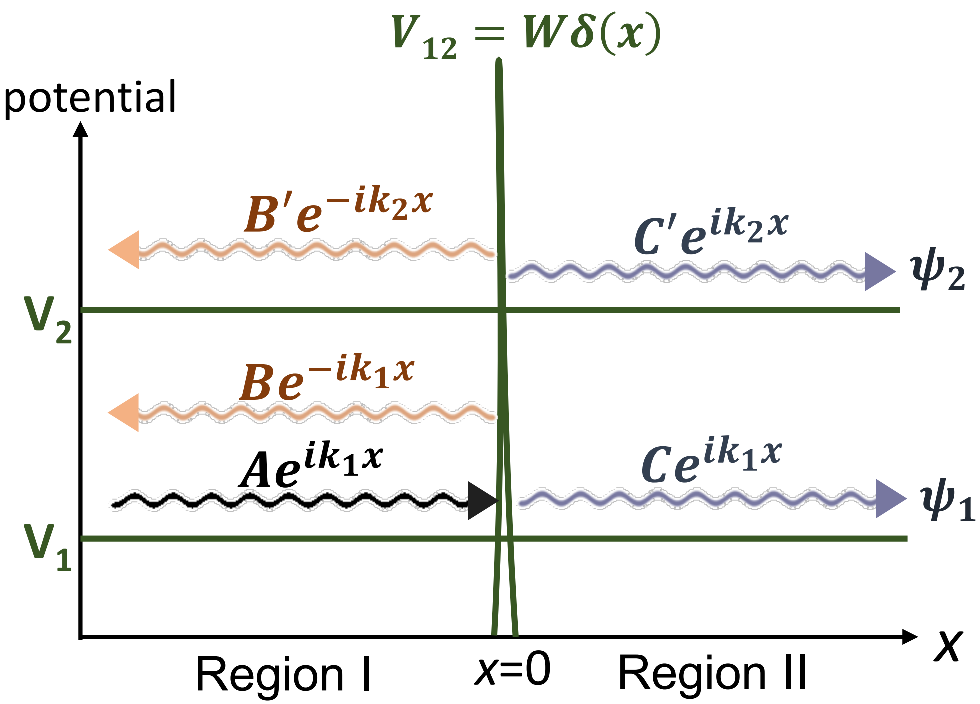
- There're four breakpoints between region 0 to 4, and thus four matrix transformations in this system. Pay attention to the last transformation, where the coefficient *B'* is set to be 0

- Coefficient *A* could be set as 1 during numerical calculation, as transmission probability is only a ratio.

# Problem 2: Inelastic tunneling—electronic coupling

For the following system, use Matlab to calculate transmission probability ($T = \frac{|C|^2}{|A|^2}$) of $\psi_1$ by solving a system of linear equations of variables *A, B, C, B' and C'*

Choose $E$ = 4 eV, $V_1$ = 1 eV, $V_2$ = 3 eV, $W$ = 6




$$\psi_1 = \begin{cases} Ae^{ik_1x} + Be^{-ik_1x}, x < 0 \\ Ce^{ik_1x}, \quad x > 0 \end{cases}, \quad \psi_2 = \begin{cases} B'e^{-ik_2x}, x < 0 \\ C'e^{ik_2x}, x > 0 \end{cases}$$

**Inelastic: energy loss**

- This model involves coupling between two electronic states
- Coupling term: $V_{12}$

Schrödinger Equation: $H\psi = E\psi$

where: $\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix}, H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix}$

$$H_{ii} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_i, \; i = 1,2$$

$$H_{12} = H_{21} = V_{12} = W\delta(x)$$

About the Schrödinger Equation:

$$\begin{pmatrix} -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_1 & W\delta(x) \\ W\delta(x) & -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}+V_2 \end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}=\begin{pmatrix}E_1 & 0\\ 0 & E_2\end{pmatrix}\begin{pmatrix}\psi_1\\ \psi_2\end{pmatrix}$$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2\psi_1(x)}{dx^2}+V_1\psi_1(x)+\boxed{W\delta(x)\psi_2(x)}=E_1\psi_1(x)$$

Coupling term comes in

$$\lim_{\varepsilon\to 0}\int_{-\varepsilon}^{\varepsilon}\left[-\frac{\hbar^2}{2m}\frac{d^2\psi_1}{dx^2}+(V_1-E_1)\psi_1(x)+W\delta(x)\psi_2(x)\right]dx$$

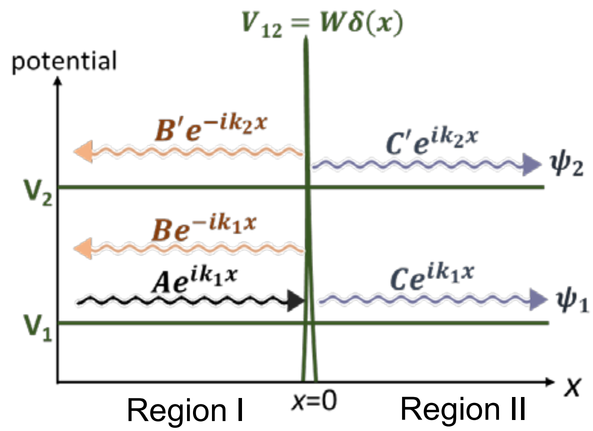
$$=\lim_{\varepsilon\to 0}\left[-\frac{\hbar^2}{2m}\frac{d\psi_1}{dx}\bigg|_{-\varepsilon}^{\varepsilon}+2\varepsilon(V_1-E_1)_1\psi_1(0)+W\psi_2(0)\right]$$

$$=-\frac{\hbar^2}{2m}\left(\frac{d\psi_1^{II}}{dx}\bigg|_{x=0}-\frac{d\psi_1^{I}}{dx}\bigg|_{x=0}\right)+W\psi_2(0)=0$$

Boundary Conditions:

$$\psi_1^I(0) = \psi_1^{II}(0) \quad \Rightarrow A + B = C \qquad ①$$

$$\psi_2^I(0) = \psi_2^{II}(0) \quad \Rightarrow B' = C' \qquad ②$$




From Schrödinger Equations:

$$-\frac{\hbar^2}{2m}\left[\left.\frac{d\psi_1^{II}}{dx}\right|_{x=0} - \left.\frac{d\psi_1^{I}}{dx}\right|_{x=0}\right] + W\psi_2(0) = 0 \qquad ③$$

$$-\frac{\hbar^2}{2m}\left[\left.\frac{d\psi_2^{II}}{dx}\right|_{x=0} - \left.\frac{d\psi_2^{I}}{dx}\right|_{x=0}\right] + W\psi_1(0) = 0 \qquad ④$$

Hint: Above we've derived four linear equations of five variables (*A, B, C, B', C'*). Set A=1, then the rest of the variables can be solved via Matlab.

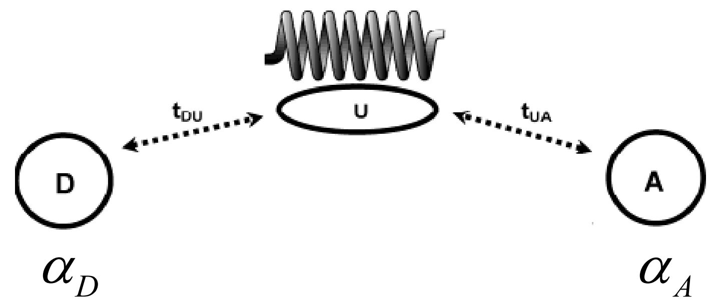
Thus the transmission probability would be readily obtained by: $T = \frac{|C|^2}{|A|^2}$

# Problem 3: Inelastic tunneling—electron-nuclear coupling

1. Develop a Matlab script (may involve if-else construct) to evaluate the matrix elements of $\hat{H}^{e/n}$, i.e. $\langle n|(a^\dagger + a)|q\rangle$, when $n, q \in [0,4]$, and express them in a matrix form.
2. Choose $T$ = 300 K, $t_{DU} = t_{UA} = 0.2$ eV, $\hbar\omega_U = 0.1$ eV, $\alpha_U - \alpha_D = 1$ eV($\alpha_A$ and $\alpha_D$ are related by $E_i = E_f$), plot $k_{ET}$ vs $\gamma_U$ in the range $\gamma_U$=0~0.3 eV for both elastic tunneling (n=q=0) and inelastic tunneling (n=0, q=1)

Differences from problem 2:

- Energy is lost via electron-oscillator vibronic interaction i.e., it involves both electronic and vibrational degrees of freedom
- Wavefunctions $\psi$ are bound states, rather than plane waves




Initial states and final states:

$$|i\rangle = |\varphi_D; n\rangle, |f\rangle = |\varphi_A; q\rangle$$

$\varphi_{D,A}$: Wavefunction of electronic part

*n, q*: Quantum number of harmonic oscillator (vibronic part)

Initial and final energy (should be equal)

$$E_i = \alpha_D + (n + 1/2)\hbar\omega_U = E_{tun}$$

$$E_f = \alpha_A + (q + 1/2)\hbar\omega_U$$

$$\boxed{E_i = E_f}$$

Model Hamiltonian:

$$\hat{H}^{bridge} = \hat{H}^{e}_{site} + \hat{H}^{n} + \hat{H}^{e/n}$$

where: $\hat{H}^{e}_{site} = \alpha_U |\varphi_U\rangle\langle\varphi_U|$

Harmonic Oscillator Hamiltonian $\hat{H}^{n} = \left(a^\dagger a + \frac{1}{2}\right)\hbar\omega_U$

Electronic-vibronic interaction $\hat{H}^{en} = \gamma_U (a^\dagger + a)|\varphi_U\rangle\langle\varphi_U|$

$\gamma_U$: coupling strength

Reference: *J. Phys. Chem. B* **2004,** *108,* 15511-15518

Bridge's Green's function: $\hat{G}^{bridge} = \hat{G}_0^{\ bridge} + \hat{G}_0^{\ bridge} \hat{H}^{e/n} \hat{G}_0^{\ bridge}$

where $\hat{G}_0^{\ bridge}\left(E_{tun}\right) = \dfrac{1}{E_{tun} - \hat{H}^{bridge}} = \sum_m \dfrac{\left|\varphi_U ; m\right\rangle\left\langle \varphi_U ; m\right|}{\alpha_D - \alpha_U}$

## Transmission matrix elements are:

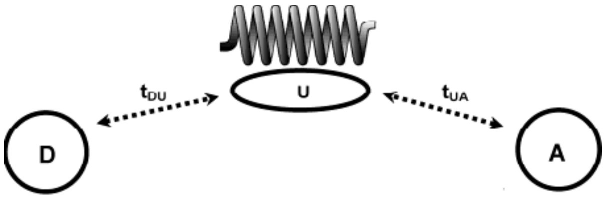
- Elastic tunneling (*n*=*q*)

$$T_{DA}^{nn} = \left\langle \varphi_D ; n \right| \hat{G}_0^{\ bridge} \left| \varphi_A ; n \right\rangle = \frac{t_{DU} t_{UA}}{\alpha_D - \alpha_U}, \quad \text{where} \ \ t_{ij} = \left\langle \varphi_i \middle| \varphi_j \right\rangle$$

- Inelastic tunneling (*n*≠*q*)

$$T_{DA}^{nq} = \left\langle \varphi_D ; n \right| \hat{G}_0^{\ bridge} \hat{H}^{e/n} \hat{G}_0^{\ bridge} \left| \varphi_A ; q \right\rangle$$

$$= \frac{t_{DU} t_{UA} \gamma_U}{\left(\alpha_D - \alpha_U\right)\left(\alpha_A - \alpha_U\right)} \left\langle n \right| a^{\dagger} + a \left| q \right\rangle$$




## Electron transfer rate:

$$k_{ET} = \frac{2\pi}{\hbar} \left| T_{DA}^{if} \right|^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left( -\frac{\lambda^2}{4\pi\lambda k_B T} \right), \quad \text{where} \ \ \lambda = \gamma_U^{\ 2} / \hbar\omega_U$$

*Reference: J. Phys. Chem. B* **2004,** *108,* 15511-15518

About $\langle n|(a^\dagger + a)|q\rangle$:

- These notations are adapted from quantum harmonic oscillator system
- $\{|n\rangle\}$ are the orthonormal eigenstates of the Hamiltonian of harmonic oscillator $\widehat{H}^n = \left(a^\dagger a + \frac{1}{2}\right)\hbar\omega_U$, with quantum number *n* (*n*=0, 1, …)
- $a^\dagger, a$ are called "creation" and "annihilation" operators, with the following relationship:

$$a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle, \qquad a|n\rangle = \sqrt{n}|n-1\rangle$$

- Because $\{|n\rangle\}$ are orthonormal, so

$$\langle n|a^\dagger|m\rangle = \sqrt{m+1}\langle n|m+1\rangle = \sqrt{m+1}\delta_{n,m+1}$$
$$\langle n|a|m\rangle = \sqrt{m}\langle n|m-1\rangle = \sqrt{m}\delta_{n,m-1}$$

- More detailed description can be found in http://en.wikipedia.org/wiki/Quantum_harmonic_oscillator , under “ladder operator method” section