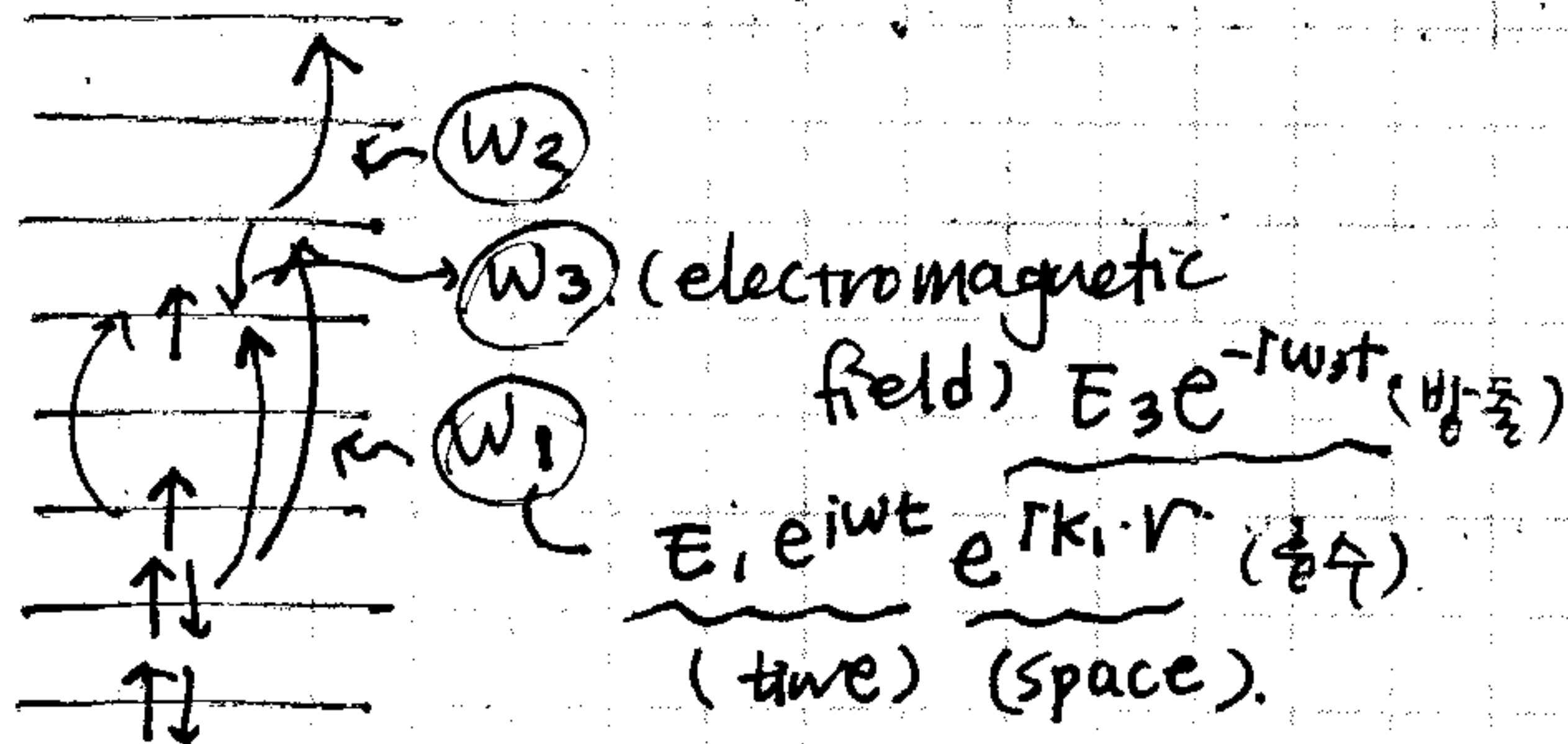


1. HF CI theory  
 Perturbation theory.

2. Van der Waals interaction in solid: vibration frequency  $\omega$  is small  
 No class on Mon, Wed.



$$H = H_0 + V(t) \Rightarrow i\hbar \frac{\partial \psi}{\partial t} = H\psi = E\psi$$

$\downarrow$   
 $(H_0 + V(t))$   
 $\downarrow$

$$i\hbar \frac{\partial \psi_0}{\partial t} = H_0 \psi_0 \Rightarrow i\hbar \frac{\partial u_0(t, t_0) \psi_0(t_0)}{\partial t} = H_0 u_0(t, t_0) \psi_0(t_0)$$

Sol)  $\psi_0(t, t_0) = u_0(t, t_0) \psi_0(t_0)$

$$i\hbar \frac{\partial u_0(t, t_0)}{\partial t} = H_0 u_0(t, t_0) \Rightarrow u_0(t, t_0) = \exp\left(\frac{H_0}{i\hbar}(t - t_0)\right)$$

$$i\hbar \frac{\partial u(t, t_0)}{\partial t} = [H_0 + V(t)] u(t, t_0) \psi_0(t_0)$$

$$i\hbar \frac{\partial u(t, t_0)}{\partial t} = [H_0 + V(t)] u(t, t_0)$$

$$u(t, t_0) = u_0(t, t_0) + \left(\frac{1}{i\hbar}\right) \int_{t_0}^t dt_1 [u_0(t_1, t_0) \times V(t_1) \times u(t_1, t_0)]$$

$$i\hbar \left[ \frac{\partial u_0}{\partial t} + \frac{1}{i\hbar} u_0(t, t_0) V(t) u(t, t_0) \right]$$

$$i\hbar \frac{\partial u_0}{\partial t} = H_0 u_0$$

$$i\hbar \left[ \frac{H_0 u_0}{i\hbar} + \frac{V \cdot u(t, t_0)}{i\hbar} \right]$$

$$= (H_0 + V) u(t, t_0)$$

$$\left[ \because i\hbar \frac{\partial u_0(t, t_0)}{\partial t} = H_0 u_0(t, t_0) \right]$$

$$= i\hbar \frac{\partial u(t, t_0)}{\partial t} = H_0 u(t, t_0) \quad ]$$

$$i\hbar \frac{\partial u(t, t_a)}{\partial t} = [H_0 + V(t)] u(t, t_a)$$

$$\Rightarrow u(t, t_a) = \underbrace{u_0(t, t_a)}_{\text{exp}(\frac{iH_0}{\hbar}(t-t_a))} + \frac{1}{i\hbar} \int_{t_a}^t u_0(t, t_1) V(t_1) \underbrace{u(t_1, t_a)}_{u_0(t_1, t_a) + O} dt_1$$

$$u(t, t_a) = u_0(t, t_a) + \left(\frac{1}{i\hbar}\right) \int_{t_a}^t V_0(t, t_1) V(t_1) u_0(t_1, t_a) dt_1$$

$$+ \left(\frac{1}{i\hbar}\right)^2 \int_{t_a}^t \int_{t_a}^{t_1} dt_1 dt_2 [u_0(t, t_2) V(t_2) u_0(t_2, t_1) V(t_1) u_0(t_1, t_a)]$$

$$+ \left(\frac{1}{i\hbar}\right)^3 \int_{t_a}^t \int_{t_a}^{t_1} \int_{t_a}^{t_2} dt_1 dt_2 dt_3 [u_0(t, t_3) V(t_3) u_0(t_3, t_2) V(t_2) u_0(t_2, t_1) V(t_1) u_0(t_1, t_a)]$$

$$u(t, t_a) = u_0(t, t_a) + \underbrace{u_0^{(1)}(t, t_a)}_{\text{single transition}} + \underbrace{u_0^{(2)}(t, t_a)}_{\text{double transition}} + \dots$$

$$u_0^{(k)} = \left(\frac{1}{i\hbar}\right)^k \int_{t_a}^t \int_{t_a}^{t_1} \dots \int_{t_a}^{t_{k-1}} dt_1 dt_2 \dots dt_k [u_0(t, t_k) V(t_k) u_0(t_k, t_{k-1}) V(t_{k-1}) u_0(t_{k-1}, t_{k-2}) \dots V(t_1) u_0(t_1, t_a)]$$

$$t > t_1 > t_2 > \dots > t_k > t_a$$

$$u_0^{(5)}(t, t_a) = \left(\frac{1}{i\hbar}\right)^5 \int_{t_a}^t \int_{t_a}^{t_1} \int_{t_a}^{t_2} \int_{t_a}^{t_3} \int_{t_a}^{t_4} dt_5 dt_4 dt_3 dt_2 dt_1$$

$$[u \ v \ u \ v \ u \ v \ u \ v \ u \ v \ u]$$

$$\psi(t, t_a) = u(t, t_a) |n\rangle$$

$$= \sum_K |K\rangle \langle K | u(t, t_a) |n\rangle$$

$$H = H_0 - P \cdot E(t)$$

$$\hookrightarrow |E\rangle e^{i(k \cdot r)} e^{iE t / \hbar}$$

$$\psi(t, t_a) = \frac{1}{i\hbar} \int_{t_a}^t dt_1 \exp\left(\frac{iE_1}{\hbar}(t-t_1)\right) \frac{1}{\hbar} \langle K | V(t_1) |n\rangle \exp\left(\frac{iE_n}{\hbar}(t-t_1)\right) u_0(t, t_1) |n\rangle$$

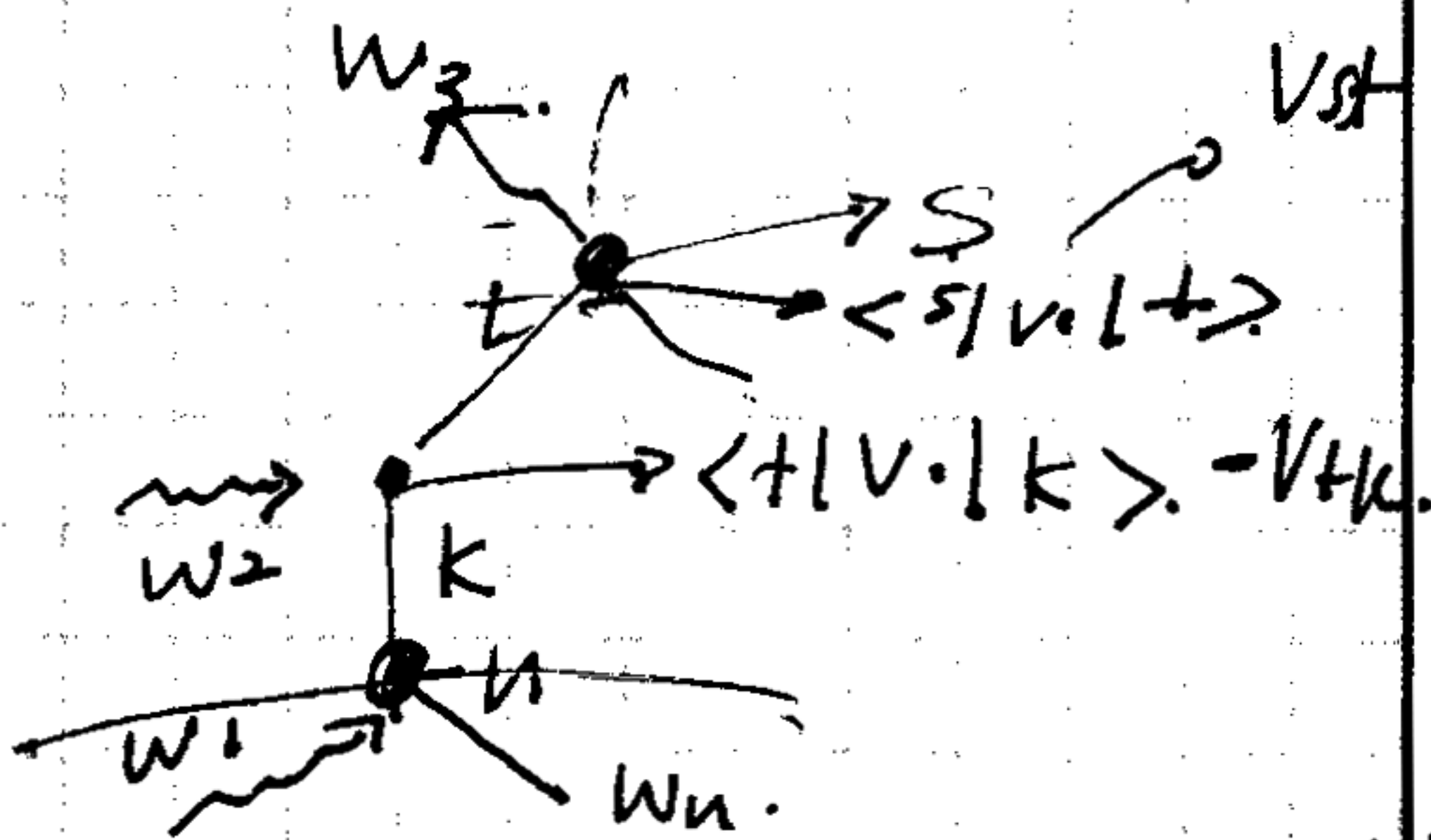
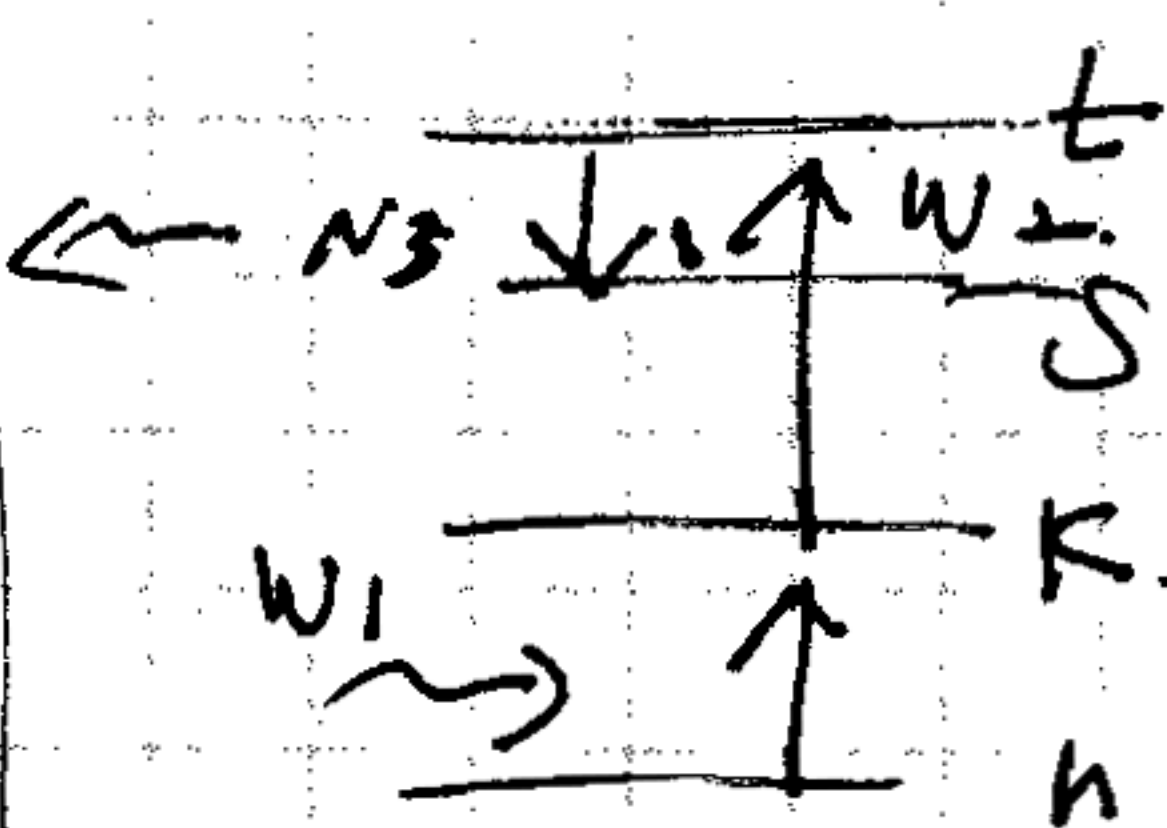
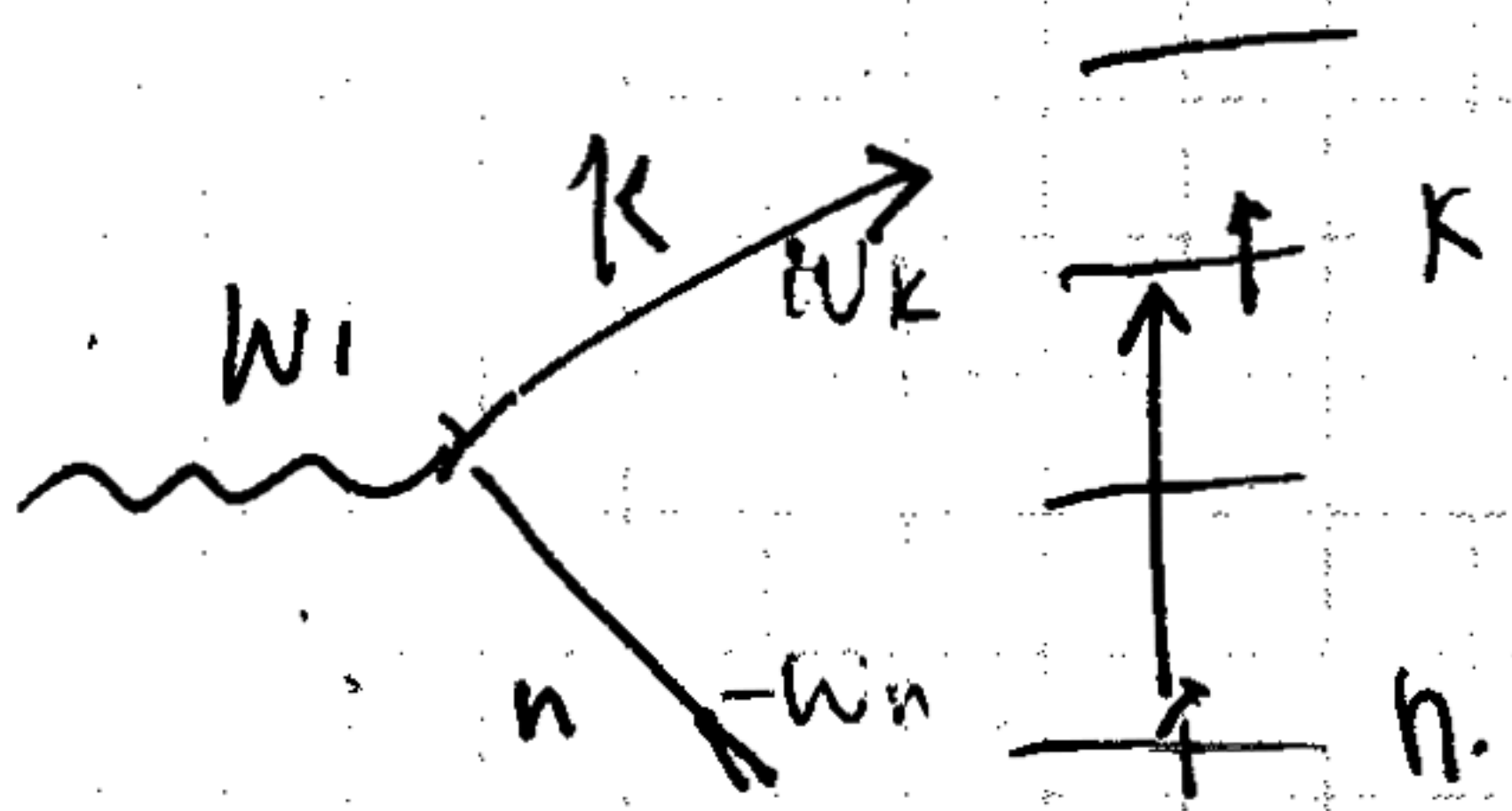


Transition  $\frac{E^2}{\hbar^2}$

$$\psi^k(t+a) = \left(-\frac{E}{\hbar}\right) \int_0^t dt_1 \left[ \exp^{+i(\omega_k - \omega_n + \omega_1)t_1} \right] \exp^{-i\omega_k t} \cdot \exp^{+i\omega_n t_1}$$

$$= E \cdot P = V_0 \frac{\exp^{i(-\omega_n + \omega_k)t} - \exp^{-i\omega_k t}}{\omega_k - \omega_n + \omega_1}$$

$$= \left(\frac{1}{i\hbar}\right) \langle k | V_0 | k \rangle \frac{\exp^{i(-\omega_n + \omega_k)t} + e^{-i\omega_k t}}{\omega_k - \omega_n + \omega_1} | k \rangle$$



$$\psi^3(t,0) = \langle s | \psi^2(t,0) | n \rangle$$

$$\left(\frac{1}{i\hbar}\right) V_{3+} V_{k+} V_{kn} | s \rangle \frac{\exp^{i(-\omega_n - \omega_1 + \omega_3)t} - e^{-i\omega_k t}}{\hbar(-\omega_1 - \omega_n + \omega_k)(-\omega_1 - \omega_n - \omega_3 + \omega_k)}$$

MPT.