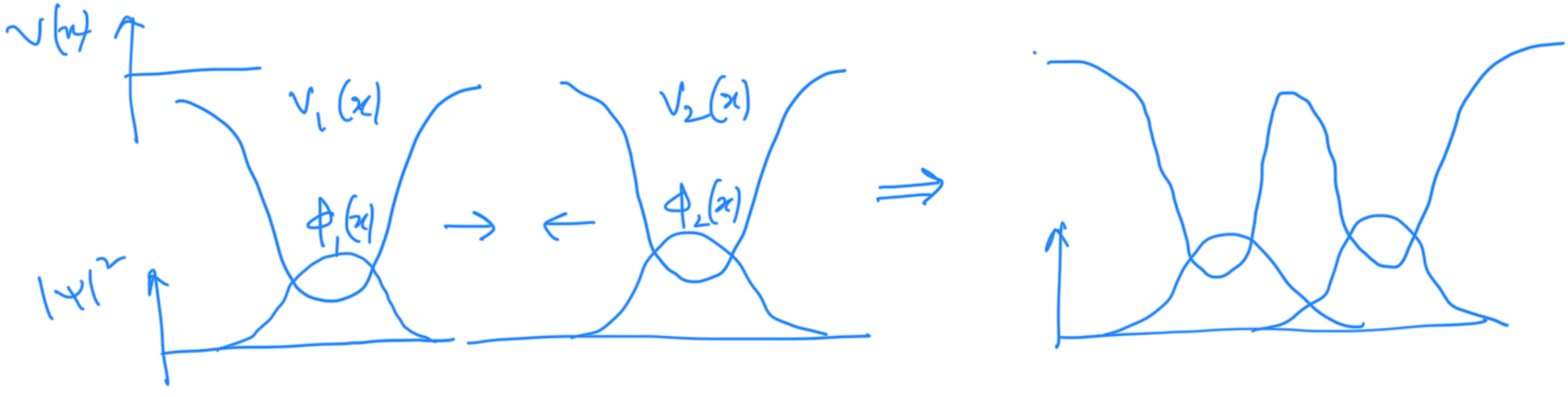
Two atoms in proximity



Let two atoms each having one electron approaching each other from infinity.

It is essentially a two electron problem which we can solve at different levels of accuracy with commensurate levels of rigour.

Simplest way to approximately solve it is to completely neglect their mutual interaction. Both the electrons would then be subjected to the same Hamiltonian $\boxed{H = T + V_1(r) + V_2(r)}$. but would occupy two different states to honour Pauli Exclusion.

The two electrons then moves completely independent of each other, as if the other electron does not exist.
We therefore need a simple diagonalization of the $\hat{H}$ in a suitable basis.

Let: $\hat{H}_1\psi_1 = E_0\psi_1$; $H_1 = -\frac{\hbar^2}{2}\frac{\partial}{\partial x^2} + V_1(x)$

$H_2\psi_2 = E_0\psi_2$; $H_2 = -\frac{\hbar^2}{2}\frac{\partial}{\partial x^2} + V_2(x)$

Although $\langle\psi_1|\psi_2\rangle \neq 0$ but small
We approximate $\langle\psi_1|\psi_2\rangle = 0$

$\therefore \hat{H}$ in $\{\psi_1(x), \psi_2(x)\}$ basis:

$$\begin{bmatrix} \langle\psi_1|H|\psi_1\rangle & \langle\psi_1|H|\psi_2\rangle \\ \langle\psi_2|H|\psi_1\rangle & \langle\psi_2|H|\psi_2\rangle \end{bmatrix} = \begin{bmatrix} E_0+\alpha & t \\ t & E_0+\alpha \end{bmatrix} \Rightarrow \begin{bmatrix} E_1 & t \\ t & E_1 \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$$

$\Rightarrow E = E_1 + t \rightarrow \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 1 \\ 1 \end{bmatrix} \Rightarrow \psi = \frac{1}{\sqrt{2}}[\psi_1(x) + \psi_2(x)] \Rightarrow$ 

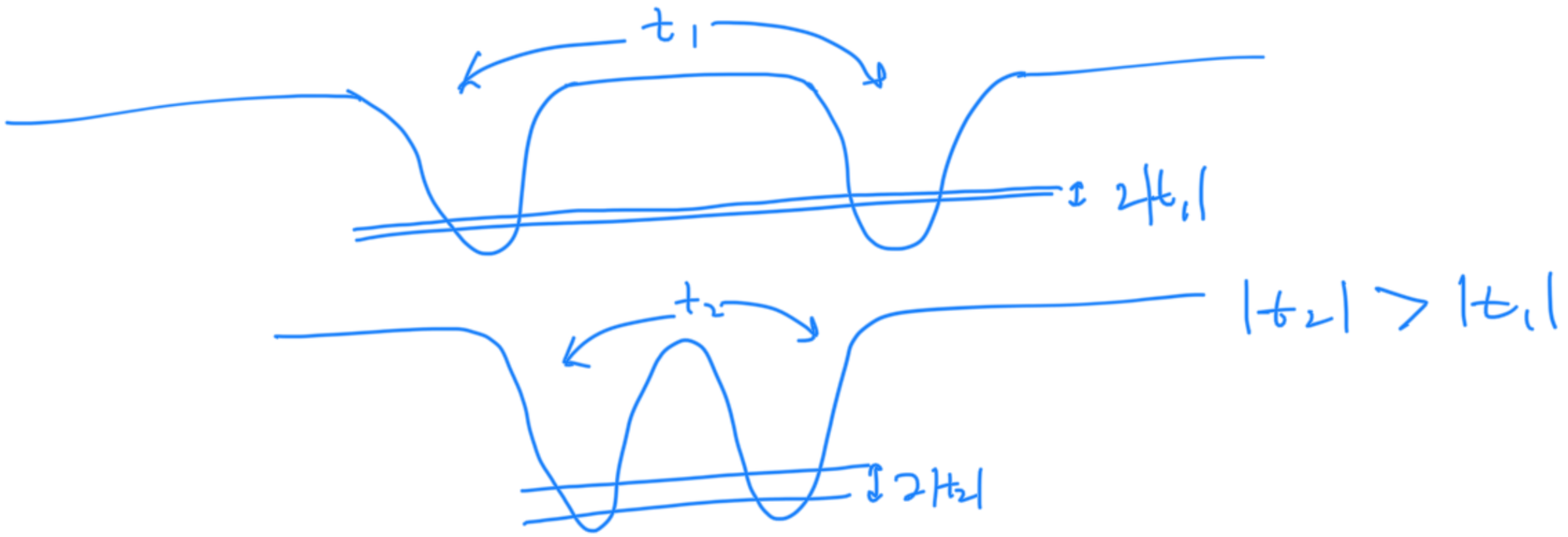
$E = E_1 - t \rightarrow \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} \pm 1 \\ \mp 1 \end{bmatrix} \Rightarrow \psi = \frac{1}{\sqrt{2}}[\pm\psi_1(x) \mp \psi_2(x)] \Rightarrow$ 

t: $\langle\psi_1|(T + V_1 + V_2)|\psi_2\rangle$

$= [\langle\psi_1|(T+V_1)|\psi_2\rangle + \langle\psi_1|V_2|\psi_2\rangle]$

$= [E_0\langle\psi_1|\psi_2\rangle + \langle\psi_1|V_2|\psi_2\rangle] < 0 \rightarrow t$ is -ve

E_0: -ve; $\langle\psi_1|\psi_2\rangle$: +ve; $\langle\psi_1|V_2|\psi_2\rangle$: +ve



We can improve the description by assuming that each of the electrons feel an average effect of all the other electrons.

In such "average effect of the other electrons" each electron still move independent of each other as a single particle.

Such a picture is thus called the "single particle" picture

In fact, it turns out to be quite realistic to invoke such "average effect of all other electrons" and renormalize many electron problems in effect to a single electron problem.

$$\Rightarrow \quad H = T + V_1(r) + V_2(r) + \bar{V}_{ee}(r)$$

$\bar{V}_{ee}(r)$ is the "average effect of all other electrons".

Making a good approximation for $\bar{V}_{ee}(r)$ has remained an active area of research for over 50 years now.

In fact, Walter Kohn in 1965, (Nobel in Chem 1998) showed that any many electron problem can be "exactly" renormalized to a single electron problem when the $\bar{V}_{ee}(r)$ has to be a functional of the charge density $\rho(r) = \sum_{\text{occupied states}} |\psi_i(r)|^2$ where $\{\psi(r)\}$ are the single particle states.

→ Density functional theory (DFT).

However DFT does NOT give any guidance to derive any functional which can be universally applied to all materials. It just says that it "exists".

Neglecting $V_{ee}(r)$ is thus the simplest single particle picture.

Returning back to the simplest picture of <u>atoms in proximity</u>.

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Condensed Matter.

$\rightarrow$

$$\begin{bmatrix} E_0 & t & t' \\ t & E_0 & t \\ t' & t & E_0 \end{bmatrix}$$

$|t'| < |t|$

Assume No overlap of ϕ_1 and ϕ_3

$\Rightarrow t' \rightarrow 0$

$\therefore$

$\rightarrow$

$$\begin{bmatrix} E_0 & t & 0 & 0 \\ t & E_0 & t & 0 \\ 0 & t & E_0 & t \\ 0 & 0 & t & E_0 \end{bmatrix}$$