

Tight binding method for electronic structure.

Unlike a metal: In the case of dielectrics and insulators we can and should start with atomic like orbitals for electrons.

So the ground state can be expanded as:

$$\Psi(\vec{r}) = \sum_n \sum_{\alpha} \phi_{n,\alpha} \varphi_{\alpha}(r-R_n)$$

$\varphi_{\alpha}(r-R_n)$  are atomic orbitals

$\alpha$  - a full set of the corresponding quantum numbers

$\phi_n$  need to be determined.

This starting condition is called the Tight-Binding method or LCAO.

To follow a more modern notation, let's introduce the Dirac notation, i.e.

$$\varphi_{\alpha}(r-R_n) \equiv |R_n, \alpha\rangle$$

The Sch. equation now can be written as:

$$\hat{H} \Psi(r) = E \Psi(r)$$

$$\sum_n \sum_{\alpha} \langle R_m, \beta | \hat{H} | R_n, \alpha \rangle \phi_{n,\alpha} = E \sum_n \sum_{\alpha} \langle R_m, \beta | R_n, \alpha \rangle \phi_{n,\alpha}$$

the overlap integrals.

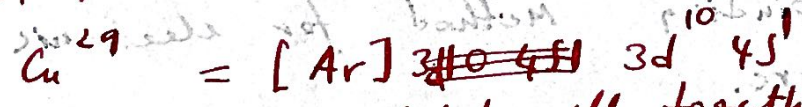
Here is the main problem:

The size of the matrix depends on the of sites  $n$  and orbitals we want to include.

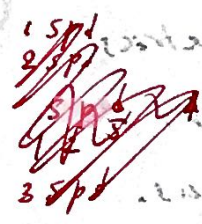


L13

Let me illustrate this for Cu:



or 15 orbitals all together



Electrons completely fill in the shells with  $n=1, 2, 3$  while for  $n=4$  it is partially occupied by 1 electron.

So if  $N$  is the total number of atoms in the crystal we have  $15N \times 15N$  matrixes!

However, we can use few physical ideas to simplify the whole story (e.g.)

Since the overlap between the valence and core electrons is almost 0 the matrix reduces to:

$$\begin{pmatrix} \boxed{\text{Core}} & 0 \\ 0 & \boxed{\text{Valence}} \end{pmatrix}$$

and in practice those can be treated as independent solutions.

Note: For strongly correlated electrons  $d$ -electrons are not too localized (unlike heavy fermions with  $f$ -electrons) so one need to introduce some overlap between the core states and the valence ones.

Another Note: We can use the same  $\begin{pmatrix} \boxed{C} \\ \boxed{V} \end{pmatrix}$  for exciting states but now the valence electron states will be extended to include the excited states.

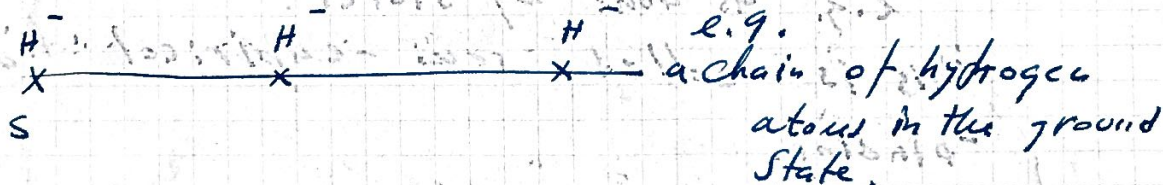


Let's study the simplest case of s-electrons on a 1D chain.

$$\sum_n [\langle R_m | H | R_n \rangle - E \langle R_m | R_n \rangle] \phi_n = 0$$

$\langle R_m | R_n \rangle = \delta_{mn}$  so we get

$$\sum_n (\langle R_m | H | R_n \rangle - E \delta_{mn}) = 0$$



To calculate  $\langle R_m | H | R_n \rangle$  we use an explicit form of the hamiltonian  $H$ :

$$H = \frac{\hbar^2}{2m} \nabla^2 + \sum_n V(r - R_n)$$

two cases

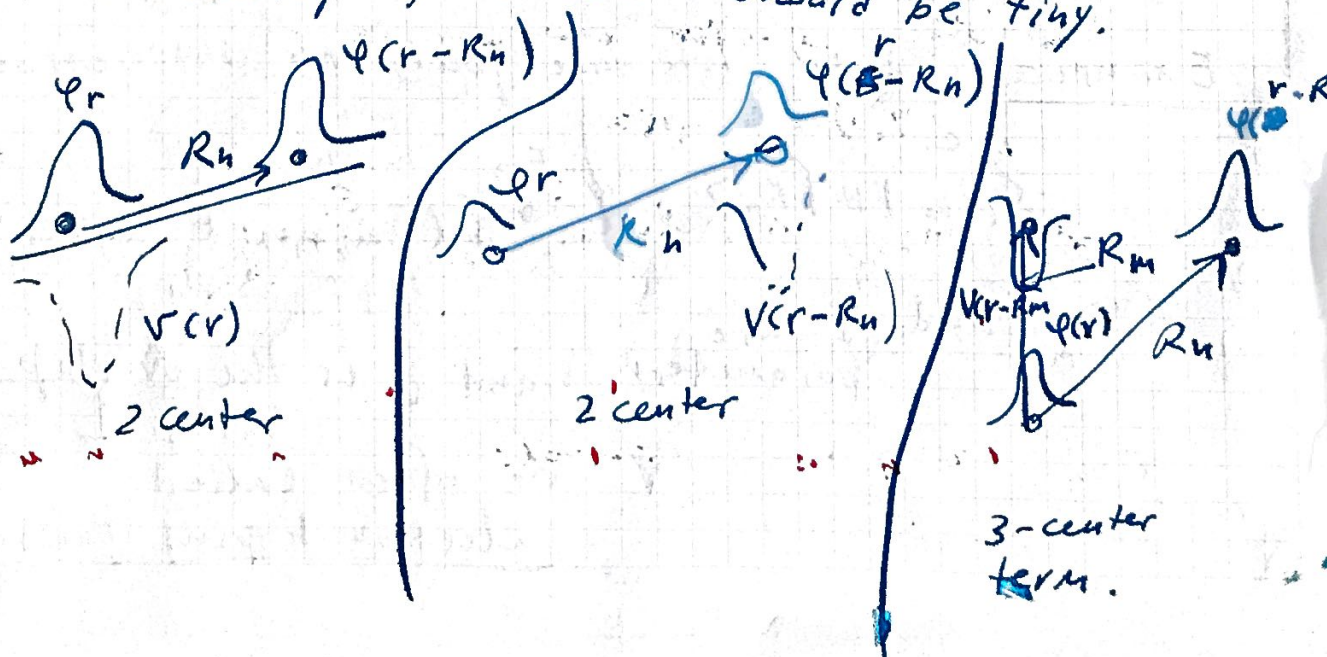
$$\langle R_m | H | R_m \rangle = \langle R_m | V(r - R_m) | R_m \rangle$$

$$\langle R_m | H | R_n \rangle = \langle R_m | V(r - R_n) | R_m \rangle \quad n \neq m$$

1-center  
2-center

and 3 centered site  $\langle R_m | V(r - R_n) | R_n \rangle$

The overlap for 3-center should be tiny.





Notes: Matrix elements hard to compute.

e.g. often no analytical forms are known

Much more popular approach:

Consider the matrix elements as parameters and fit them to the expt. values

e.g. as done by Slater.

this is called semi-empirical tight-binding.

### SLATER APPROACH

Procedure

Step 1: Begin with

$$\sum_n \left[ \langle R_m | H | R_n \rangle - E \langle R_m | R_n \rangle \right] \psi_n = 0$$

S2. Compute  $\langle R_m | H | R_n \rangle$

S3. Select Boundary conditions (b.c.)

S4. Solve for  $E$  and  $\psi_n$ ; pay attention to the allowed values based on S3.

S5. Compose the w.f. as:  $\psi(r) = \sum_n \sum_\alpha \psi_n \alpha \phi_\alpha(r - R_n)$

EXAMPLE: Lets introduce (only)  $n$ -th interaction

i.e.

$$\langle R_m | H | R_n \rangle = \begin{cases} E_0 & m=n \\ \gamma (\delta_{m,n+1} + \delta_{m,n-1}) & \text{if } m \neq n \end{cases}$$

$E_0$  and  $\gamma$  are parameters

and  $\gamma$  is the overlap integral

or often called electron hopping parameter.



Note: on surface or the interface  $E_0$  and  $\gamma$  will be special!

insert those into the

$$\sum_n \left( \langle R_n | H | R_n \rangle - E \delta_{nm} \right) \phi_n = 0$$

$$E_0 \phi_n + \gamma (\phi_{n+1} + \phi_{n-1}) = E \phi_n \quad n=1, 2, 3, \dots$$

Lets introduce the simplest boundary cond.

$$\phi_0 = 0$$

$$\phi_{N+1} = 0$$



Let's try  $\phi_n = A e^{\pm i k n a}$

$$E_0 A e^{\pm i k n a} + \gamma A \left( e^{\pm i k (n+1) a} + e^{\pm i k (n-1) a} \right) = E A e^{\pm i k n a}$$

$$E_0 + \gamma \left( e^{\pm i k a} + e^{\mp i k a} \right) = E(k)$$

$$E(k) = E_0 + 2\gamma \cos(ka)$$

which is not good

b/c. of the boundary cond since  $\cos(t)$

but  $\phi_n = A \sin(k n a)$  is better.

$$\phi_0 = A \sin(0) = 0 \quad \phi_{N+1} = A \sin(k(N+1)a) = 0$$

$$k(N+1)a = 2\pi \ell \Rightarrow k = \frac{2\pi \ell}{a(N+1)}$$

$$A = \sqrt{\frac{2}{N+1}}$$

$$\psi_n = \sum_{\ell} \phi_n$$

$$\psi_n = \sqrt{\frac{2}{N+1}} \sum_{\ell} \sin\left(\frac{2\pi \ell}{N+1} n\right) |R_n\rangle \quad \ell=1, \dots, N$$

Note this calculation is repeated in a more concise way in L14 p1-3.

Skip if you want

$E_0 \neq$  free energy of the atom  
 since we need to include potential from all other atoms called the crystal field

$\gamma$  contains very important information

lets calculate the difference between  $l=1$  and the highest  $l=N$

$$\Delta E = E_N - E_1 = -2\gamma \left[ \cos\left(\frac{N\pi}{N+1}\right) - \cos\left(\frac{\pi}{N+1}\right) \right]$$

for  $N \rightarrow \infty$   $\cos\left[\frac{\pi N}{N+1}\right] \approx \cos\left[\pi - \frac{\pi}{N+1}\right]$

and after Taylor expansion in  $\frac{1}{N}$

$$\Delta E = 4|\gamma| \left( 1 - \frac{\pi^2}{N^2} + \dots \right) \Rightarrow$$

$$\frac{\Delta E}{4\gamma} = 1 - \frac{\pi^2}{N^2} + \dots$$

so for large  $N$   $\Delta E \rightarrow 4\gamma$

SKIP for L14 p1-3

This result is important for finite size nanosystems. e.g. nanocrystals or nanoparticles.

Note that calculation is repeated in L14 p1-3.