Quantum Transport:
ATOM TO TRANSISTOR

Prof. Supriyo Datta
ECE 659
Purdue University

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Lecture 12: Basis Functions: As a Computational Tool
Ref. Chapter 4.1

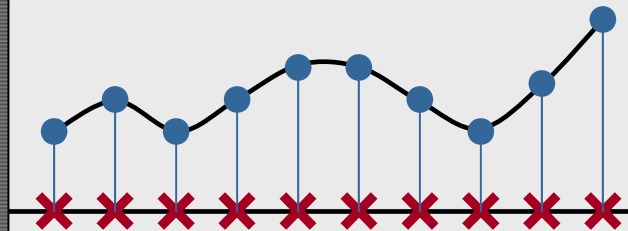*Network for Computational Nanotechnology*

What is a Basis Function?

- Next three lectures, including this one, we will concentrate on the concept of basis functions

- Very important conceptually and numerically.

- In this lecture we will concentrate on the numerical aspect.

- Schrödinger Equation: $H_{op}\Phi_\alpha = E_\alpha \Phi_\alpha$

Whereby H_{op} is converted into a matrix and Φ_α is a wavefunction represented spatially point by point

- Φ_α can be written as a linear combination of a set of basis functions: $\quad \Phi_\alpha(\vec{r}) = \sum_m \phi_m u_m(\vec{r})$

Where ϕ_m are coefficients and $u_m(\vec{r})$ are basis functions. So we can represent the wavefunction as a column vector with expansion coefficients as its elements: $\quad \Phi(\vec{r}) \rightarrow \{\phi_1 \quad \phi_2 \quad \dots \quad \dots \quad \phi_M\}^T$
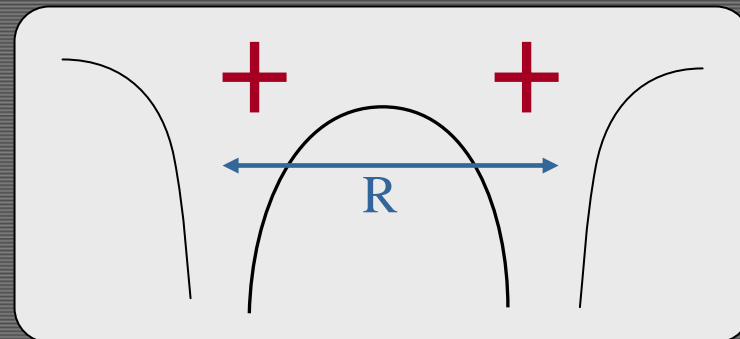
- If we choose all $u_m(\vec{r})$ such that they closely resemble the desired wave function Φ_α, we can greatly reduce the size of Hamiltonian matrix [H] and hence the total computing time

- As an example, we will illustrate how to do this with the hydrogen molecule

H_2 Potential Distribution

- Obtaining a solution to the H_2 molecule using finite difference method can be very difficult. Spherical symmetry is lacking, therefore the resulting numerical lattice can be very large and not easily implemented computationally.
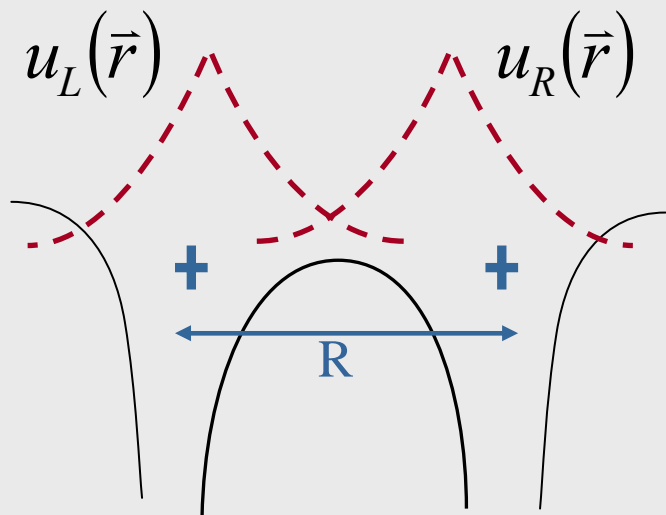
• For H$_2$ we use two basis functions: and $u_L(\vec{r})$ $u_R(\vec{r})$

• Importantly, we can now represent the Hamiltonian numerically with a 2x2 matrix rather than say a 1000x1000 matrix

H$_2$ Basis Functions

$u_L(\vec{r})$ $u_R(\vec{r})$

$+$ $+$

R

• First, lets derive the general formulation. Supposing the basis functions of $\Phi(\vec{r})$ are already known:

$$\Phi(\vec{r}) = \sum_m \phi_m u_m(\vec{r})$$

Then $E\Phi(\vec{r}) = H_{op}\Phi(\vec{r})$ becomes

$$H_{op}\sum_m \phi_m u_m(\vec{r}) = E\sum_m \phi_m u_m(\vec{r})$$

- Multiplying by $u_n^*(\vec{r})$ and integrating both sides over all r,

$$\int d\vec{r}\, u_n^*(\vec{r}) \left[H_{op} \sum_m \phi_m u_m(\vec{r}) \right] = \int d\vec{r}\, u_n^*(\vec{r}) \left[E \sum_m \phi_m u_m(\vec{r}) \right]$$

or

$$\sum_m H_{nm} \phi_m = E \sum_m S_{nm} \phi_m$$

where, $\int d\vec{r}\, u_n^*(\vec{r}) H_{op} u_m(\vec{r}) = H_{nm}$ and $S_{nm} = \int d\vec{r}\, u_n^*(\vec{r}) u_m(\vec{r})$

- Written as a matrix this becomes $[H]\{\Phi\} = E[S]\{\Phi\}$

Where [H] elements are given by H_{nm}, [S] elements by S_{nm}, and $\{\Phi\}$ elements by Φ_m

- In choosing the basis functions it is often convenient to make them orthogonal, such that $S_{nm} = \delta_{nm}$ that is, [S] is the identity matrix

Back to H$_2$

• But, in numerical calculations it is often more convenient to use non-orthogonal basis sets. For example, in H$_2$…

Basis Function Overlap in H$_2$

$u_L(\vec{r})$ overlap $u_R(\vec{r})$

$+$ $+$

R
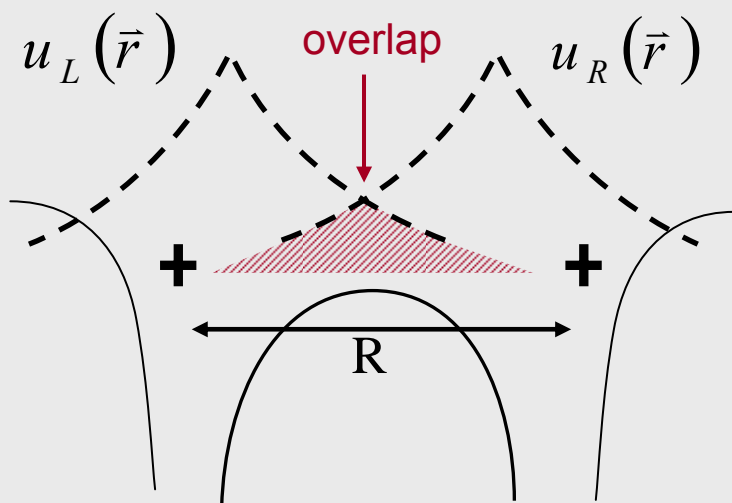
• Now, how do we use the shown general formulation to solve H$_2$?

• To begin with, excluding electron interaction, the H$_2$ Schrödinger Equation is set as:

$$H_{op}\Phi = E\Phi, \text{ where}$$

$$H_{op} = -\hbar^2\!\big/\!{2m}\nabla^2 + U_N(\vec{r}) + U_{N'}(\vec{r})$$

• And the H$_2$ basis functions are given by…

Left:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U_N(\vec{r})\right]u_L(\vec{r}) = E_0 u_L(\vec{r})$$

Right:

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + U_{N'}(\vec{r})\right]u_R(\vec{r}) = E_0 u_R(\vec{r})$$

Use these two basis functions to write:

$$\Phi(\vec{r}) = \phi_L u_L(\vec{r}) + \phi_R u_R(\vec{r})$$

So that the original Schrödinger equation reduces to a 2x2 matrix;

$$[H]\begin{Bmatrix}\phi_L\\\phi_R\end{Bmatrix} = E[S]\begin{Bmatrix}\phi_L\\\phi_R\end{Bmatrix}$$

• First, let's write the S matrix, assuming $u_L(\vec{r})$ and $u_R(\vec{r})$ are normalized, so

$$S = \begin{bmatrix}1 & s\\s & 1\end{bmatrix}$$

Where,

$$s = \int d\vec{r}\, u_L^*(\vec{r})u_R(\vec{r})$$

$$= \int d\vec{r}\, u_R^*(\vec{r})u_L(\vec{r})$$

- Now the Hamiltonian Matrix:

$$H = \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix}$$

where

$$H_{11} = \int d\vec{r} u_L^* H_{op} u_L$$

$$= \int d\vec{r} u_L^* \left[E_0 u_L + U_{N'} u_L \right]$$

let $a = \int d\vec{r} u_L^* U_{N'} u_L$

So, $H_{11} = E_0 + a$ and

$H_{22} = E_0 + a$

- Similarly,

$$H_{21} = \int d\vec{r} u_R^* H_{op} u_L$$

$$= \int d\vec{r} u_R^* \left[E_0 u_L + U_{N'} u_L \right]$$

let $s = \int d\vec{r} u_R^* u_L$

$$b = \int d\vec{r} u_R^* U_{N'} u_L$$

$$\therefore H_{21} = H_{12} = E_0 s + b$$

thus, $H = \begin{bmatrix} E_0 + a & E_0 s + b \\ E_0 s + b & E_0 + a \end{bmatrix}$

Note: Here the integrals for H$_2$ may be done analytically, but in practice it is usually done numerically. Evaluating such integrals numerically is usually the most time consuming part of the process

- To continue, let $A=E_0+a$ and $B=E_0s+b$

$$\therefore \begin{bmatrix} 1 & s \\ s & 1 \end{bmatrix}^{-1} \begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix} = E \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix}$$

Inverted, we have

$$\frac{1}{1-s^2} \begin{bmatrix} 1 & -s \\ -s & 1 \end{bmatrix} \begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix} = E \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix}$$

Multiply through

$$\frac{1}{1-s^2} \begin{bmatrix} A-sB & B-sA \\ B-sA & A-sB \end{bmatrix} \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix} = E \begin{Bmatrix} \phi_L \\ \phi_R \end{Bmatrix}$$

- Eigenvalues and Eigenvectors…

1st : Eigenvector $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$
eigenvalue
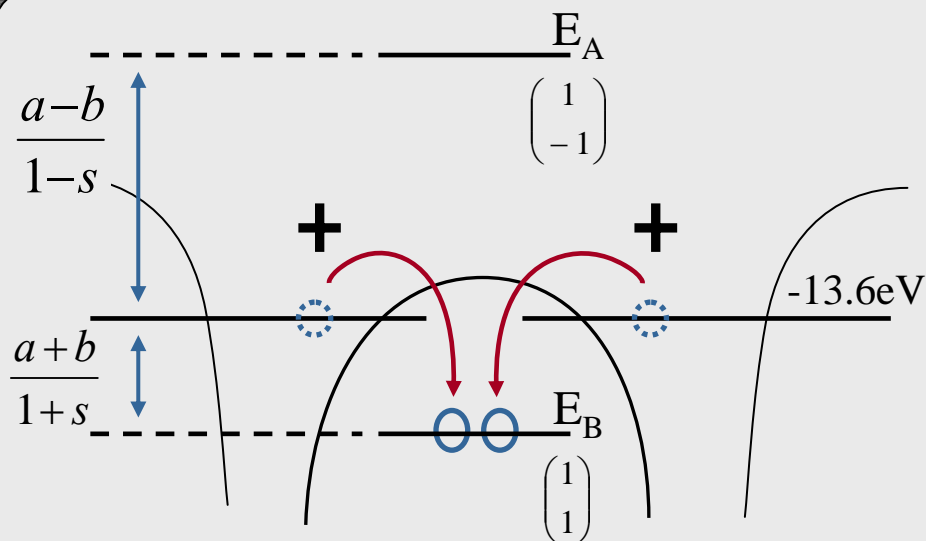
$$\frac{(A-Bs)+(B-As)}{1-s^2} = \frac{(A+B)(1-s)}{1-s^2}$$

$$= \frac{A+B}{1+s} = E_0 + \frac{a+b}{1+s}$$

2nd : Eigenvector $\begin{pmatrix} 1 \\ -1 \end{pmatrix}$
eigenvalue

$$E_0 + \frac{a-b}{1-s}$$

H$_2$ Summary

H$_2$ Schrödinger Result

$$\frac{a-b}{1-s}$$

E_A

$$\begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

+   +

-13.6eV

$$\frac{a+b}{1+s}$$

E_B

$$\begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

• When brought together, the two Hydrogen 1s levels split into bonding and anti-bonding levels. These results are remarkably close to those obtained earlier excluding Uee.
• Note: a and b are negative

• Why do we get such accurate results with only a 2x2 matrix?
Answer: The bonding level in Hydrogen is largely made up of 1s wave functions.

• How do we know that we can ignore the upper basis levels (ie.2s, 2p$_x$, 2p$_y$, 2p$_z$,etc.)? As a general rule given,

$$[S]^{-1}[H] = \begin{bmatrix} E_1 & M \\ M & E_2 \end{bmatrix}$$

If the off-diagonal elements M are << |E$_1$-E$_2$| then their effect is relatively small.