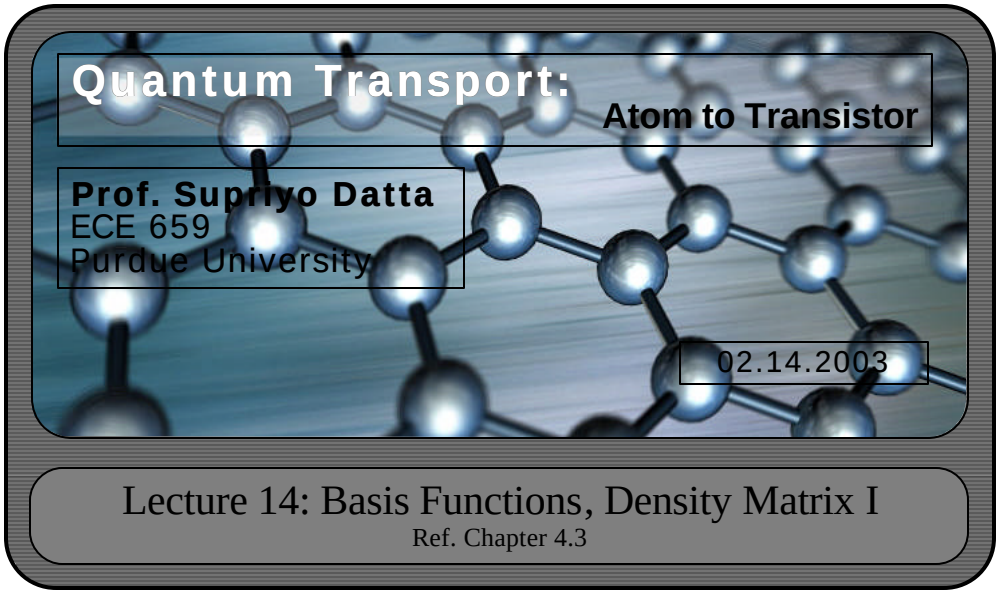


Lecture 14: Basis Functions, Density Matrix I

Ref. Chapter 4.3

Network for Computational Nanotechnology

Retouch on Concepts

00:00

• Summary of Equations:

$$E\Phi = H_{op}\Phi$$

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

$$\Phi(\vec{r}) = \sum_i f_i' u_i'(\vec{r})$$

and

$$u_i' = \sum_m C_{mi} u_m(\vec{r})$$

$$\{\Phi\} = [C]\{\Phi'\}$$

$$[A'] = C^+ AC$$

• Recall the concept of a Hilbert Space, a function space conceptually similar to a vector space. Basis functions in Hilbert space are like the unit vectors $\hat{x}, \hat{y}, \hat{z}$ in vector space.

• Proper use of basis functions facilitate matrix reduction and so are very useful computationally.

• Computationally we often use a non-orthogonal basis set (for example recall H_2). Conceptually this can cause many problems The usual procedure is to transform the oblique sets to orthogonal sets.

• From now on it will be assumed that we are working with orthogonal basis sets:

$$\int d\vec{r} u_n^* u_m = d_{mn}$$

Basis Transformations

04:08

• Basis transformations are defined by the relation:

$$u'_i = \sum_m C_{mi} u_m(\vec{r})$$

Where:

$$\Phi(\vec{r}) = \sum_m f_m u_m(\vec{r}) = \sum_i f'_i u'_i(\vec{r})$$

So to transform a vector to a new basis set we'll have:

$$\{\Phi\} = [C]\{\Phi'\}$$

• In matrix notation, basis transformations are defined by:

$$[A'] = [C]^+ A [C]$$

• To show this, we have:

$$A'_{ij} = \int d\vec{r}\, u'^*_i(\vec{r}) A_{op} u'_j(\vec{r})$$

$$= \int d\vec{r} \sum_m C^*_{mi} u^*_m(\vec{r}) A_{op} \sum_n C_{nj} u_n(\vec{r})$$

$$= \sum_m \sum_n C^*_{mi} A_{mn} C_{nj}$$

But $C^*_{mi} = (C^+)_{im}$

$$\therefore A'_{ij} = \sum_m \sum_n (C^+)_{im} A_{mn} C_{nj} = [C^+ AC]_{ij}$$

Thus, we see that C can be used to transform matrix operators as well as vectors.

Hamiltonian Matrix Transformation

• First, recall the definition of a unitary transformation:
  - Vector length is preserved
  - Proviso on unitary matrix: $C^{+}C= CC^{+} = I$

• Consider the process of finding the eigenvalues and eigenvectors of a Hamiltonian matrix.

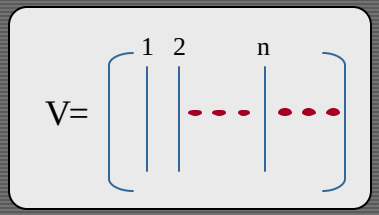
• In matlab, we invoke:

[V,D]= eig (H)

where D is a **diagonal** matrix with the eigenvalues on the diagonal and V is a square matrix with the eigenvectors as its columns.

• One way to visualize this process is to consider [H]→ [D]
as a basis transformation from the real space basis to the eigenvector basis. Formally this is expressed as:

$[D]= V^{+} [H] [V]$



Ordering of the Hamiltonian Matrix

- How do we know it is D= $V^{+}HV$ and not D=VHV^{+}?
- Look at the organization of old and new basis sets in V, H and D…

$V =$ (new basis → / old basis ↓) $H =$ (old basis → / old basis ↓) $D =$ (new basis → / new basis ↓)

- Rules of matrix multiplication require that the columns of one matrix match the rows of next matrix.
- So by observation it must be D= $V^{+}HV$

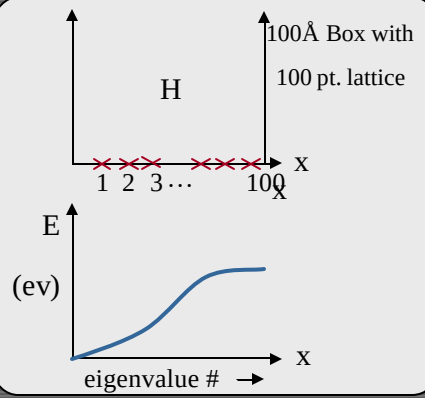
(new basis → / new basis ↓) D $=$ (old basis → / new basis ↓) $\times$ (old basis → / old basis ↓) H $\times$ (new basis → / old basis ↓)

Electrons in a Box

22:38

• As an example, we will calculate the electron density of the 'electrons in a box'

Electrons in a box



• Remember, by the method of finite differences (using box boundary conditions).

$$H = \begin{pmatrix} +2t_0 & -t_0 & & \\ -t_0 & +2t_0 & \ddots & \\ & \ddots & & \ddots \\ & & \ddots & \end{pmatrix}$$

• We want to find the electron density

$$n(x) = \sum_{occ.a} |f_a(x)|^2$$

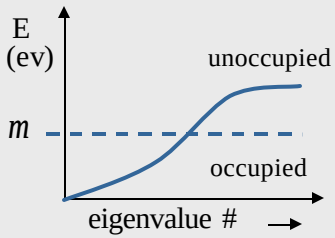
Note: 'occ. a' refers to the sum over all **occupied** states. It is very important to not that here the states are either full or empty.

Electron Density

25:48

• We can redefine n(x) by applying the Fermi function to all states. Where the Fermi function provides the "degree of occupation" between 0 and 1 of a given state at a known electrochemical potential μ.

Occupied and unoccupied levels at μ



• So the electron density is:

$$n(x) = \sum_a |f_a(x)|^2 f_a$$

$$= \sum_a f_a(x) f_a f_a^*(x)$$

• We can also re-write this as:

$$n(x) = \sum_a \sum_b f_a(x) r_{ab} f_b^*(x)$$

where

$$r_{ab} = \begin{cases} f_a & \text{if } a = b \\ 0 & \text{if } a \neq b \end{cases}$$

• Note: r_{ab} forms a diagonal matrix called the density matrix.

Density Matrix

31:00

- Generalizing we write:

$$\tilde{r}(x,x') = \sum_a \sum_b f_a(x) r_{ab} f_b^*(x')$$

Where n(x) is the diagonal of $\tilde{r}(x,x')$

- This relation can be seen to represent a unitary transformation from the eigenvector basis to **real** space. Note: $\Phi_a(x)$ are given by columns of V:

$$f_a(x) = x \begin{bmatrix} \cdots & \cdots \end{bmatrix}_{\text{a}} = V_{x,a}$$

- In other words:

$$\Phi_a(x) = (V)_{a,x}$$

$$\Phi_b^*(x') = (V^+)_{b,x'} = V_{x',b}^*$$

- Summarizing,

$$\tilde{r} = V r V^+$$

$$r = V^+ \tilde{r} V$$

- $\tilde{r}$ is in **real** space
- r is in the eigenstate space
- The diagonal elements of $\tilde{r}$ are equal to the electron density n(x).

Equilibrium Density Matrix

36:30

• So, in the eigenstate basis or "space" ? is a diagonal matrix with elements

$$f_a = \frac{1}{1+e^{(E_a - m)/k_B T}}$$

$$= f_0(E_a - m)$$

• Now in general let us denote the density matrix for any space as ?, where ? is given by:

$$r = f_0([H] - m[I])$$

• What is meant by $f_0([H] - m[I])$?

More Generally, how is the 'function' of a matrix calculated? For a diagonal matrix it is simply the 'function' operated on all elements. How about matrices with off diagonal elements?

• Example: Given [H] with off diagonal elements calculate (sin[H]). To do this we must first diagonalize [H], then operate sin () upon the diagonalized form of $[H]$, and then finally transform [H] back into its original space.

Equilibrium Density Matrix

42:00

Example: continued.

(1) Diagonalize [H]

$$\begin{pmatrix} H_1 & & \\ & H_2 & \\ & & \ddots \end{pmatrix}$$

(2) Operate sin ()

$$\begin{pmatrix} \sin(H_1) & & \\ & \sin(H_2) & \\ & & \ddots \end{pmatrix}$$

(3) Transform back to original space

$$\mathbf{V} \begin{pmatrix} \sin(H_1) & & \\ & \sin(H_2) & \\ & & \ddots \end{pmatrix} \mathbf{V^+}$$

• Note: In matlab matrix functions and element by element functions are differentiated by addition of an 'm' for matrix functions. e.g. :
sin () : represents element by element operation
sinm (): represents matrix operations.

• Finally we see the expression for ? in real space is:

$$\tilde{r} = V \begin{pmatrix} f_0(E_1 - m) & & & \\ & f_0(E_2 - m) & & \\ & & \ddots & \\ & & & f_0(E_n - m) \end{pmatrix} V^+$$

• Interestingly, ? is only diagonal in the eigenvector basis. Off diagonal elements of ? in alternate basis sets are used in some calculations, but more often than not only the diagonal elements of ? (which in any space provide electron density) are of interest.