Quantum Transport: Atom to Transistor

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Lecture 14: Basis Functions, Density Matrix I
Ref. Chapter 4.3

Network for Computational Nanotechnology
• Summary of Equations:

\[ E\Phi = H_{\text{op}}\Phi \]
\[ \Phi(\mathbf{r}) = \sum_m \phi_m u_m(\mathbf{r}) \]
\[ \Phi'(\mathbf{r'}) = \sum_i \phi'_i u'_i(\mathbf{r'}) \]

and

\[ u'_i = \sum_m C_{mi} u_m(\mathbf{r}) \]
\[ \{\Phi\} = [C]\{\Phi'\} \]
\[ [A'] = C^+ AC \]

• 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:

\[ \int d\mathbf{r} u^*_n u_m = \delta_{mn} \]
• Basis transformations are defined by the relation:

\[ u'_j = \sum_m C_{mj} u_m(\vec{r}) \]

Where:

\[ \Phi(\vec{r}) = \sum_m \Phi_m u_m(\vec{r}) = \sum_i \phi_i u'_i(\vec{r}) \]

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 \( C^*_{mi} = (C^+)_{mi} \)

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

Thus, we see that \( C \) can be used to transform matrix operators as well as vectors.
• 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:
  \[ [V,D] = \text{eig}(H) \]
  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
  as a basis transformation from the real space basis to the eigenvector basis. Formally this is expressed as:
  \[ [D] = V^* [H] [V] \]
• How do we know it is $D = V^*HV$ and not $D = VH^*$?
• Look at the organization of old and new basis sets in $V$, $H$ and $D$…

$V = \begin{pmatrix} \text{new basis} \\ \text{old basis} \end{pmatrix}$

$H = \begin{pmatrix} \text{old basis} \\ \text{old basis} \end{pmatrix}$

$D = \begin{pmatrix} \text{new basis} \\ \text{new basis} \end{pmatrix}$

• Rules of matrix multiplication require that the columns of one matrix match the rows of next matrix.
• So by observation it must be $D = V^*HV$
As an example, we will calculate the electron density of the 'electrons in a box'.

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

\[ H = \begin{pmatrix} +2t_0 & -t_0 \\ -t_0 & +2t_0 \end{pmatrix} \]

We want to find the electron density

\[ n(x) = \sum_{\text{occ.}} |\phi_\alpha(x)|^2 \]

Note: 'occ. a' refers to the sum over all occupied states. It is very important to note that here the states are either full or empty.
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 $\mu$.

So the electron density is:

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

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

We can also re-write this as:

$$n(x) = \sum_a \sum_{\beta} \phi_\alpha(x) \rho_{\alpha\beta} \phi_\beta^*(x)$$

where

$$\rho_{\alpha\beta} = \begin{cases} f_\alpha & \text{if } \alpha = \beta \\ 0 & \text{if } \alpha \neq \beta \end{cases}$$

Note: $\rho_{\alpha\beta}$ forms a diagonal matrix called the density matrix.
• Generalizing we write:
\[ \tilde{\rho}(x, x') = \sum_{\alpha} \sum_{\beta} \phi_\alpha(x) \rho_{\alpha \beta} \phi_\beta^*(x') \]
Where \( n(x) \) is the diagonal of \( \rho(x, x') \)

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

\[ \Phi_\alpha(x) = (V)_{\alpha, x} \]
\[ \Phi_\beta^*(x') = (V^+)_{\beta, x'} = V_{x', \beta}^* \]

• Summarizing,
\[ \tilde{\rho} = V \rho V^+ \]
\[ \rho = V^+ \tilde{\rho} V \]

- \( \tilde{\rho} \) is in real space
- \( \rho \) is in the eigenstate space

- The diagonal elements of \( \tilde{\rho} \) are equal to the electron density \( n(x) \).
• So, in the eigenstate basis or "space"? is a diagonal matrix with elements
\[ f_\alpha = \frac{1}{1 + e^{(E_\alpha - \mu)/k_B T}} \]
\[ = f_0 (E_\alpha - \mu) \]

• Now in general let us denote the density matrix for any space as \( \rho \), where \( \rho \) is given by:
\[ \rho = f_0 ([H] - \mu [I]) \]

• What is meant by \( f_0 ([H] - \mu [I]) \)?

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.
Example: continued.

(1) Diagonalize $[H]$

$$H = \begin{pmatrix} H_1 & \cdot & \cdot \\ H_2 & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$$

(2) Operate $\sin()$

$$\sin(H_1) \quad \sin(H_2) \quad \cdot$$

(3) Transform back to original space

$$V \begin{pmatrix} \sin(H_1) \\ \sin(H_2) \\ \cdot \end{pmatrix} V^+$$

• 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 $\rho$ in real space is:

$$\tilde{\rho} = V \begin{pmatrix} f_0(E_1 - \mu) \\ f_0(E_2 - \mu) \\ \cdot \end{pmatrix} V^+$$

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