

Quantum Transport:

Atom to Transistor

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Lecture 15: Basis Functions, Density Matrix II

Ref. Chapter 4.3 & 4.4



Network for Computational Nanotechnology



Electron Density

00:00

- Next topic shall be “Band Structure,” but before going on we will spend another lecture going over the important points of the equilibrium density matrix

- Recall, electron density is given by

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

$$\text{where } f_a = f_0(\mathbf{e}_a - \mathbf{m})$$

$$\text{and } f_0(E) = \frac{1}{e^{E/k_B T} + 1}$$

- The expression for electron density may be viewed as a special case (diagonal elements) of a much more general concept, i.e. the equilibrium density matrix:

$$[\rho] = f_0([H] - \mu[I])$$

- Note: $[\rho]$ can be written in any basis or “space,” including momentum, frequency, and 3d Cartesian coordinates. For any space the diagonal elements of $[\rho]$ will **always give the electron density.**

Function of a Matrix

05:10

- Recall, to evaluate the function of a matrix we must do the following ...

1. Given:

$$f_0 \left(\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix} \right)$$

(Note: Here, a Hermitian matrix is given, $(H^*)^T = H$. Hermitian matrices in diagonalized form contain only real numbers)

2. Diagonalize:
$$\begin{bmatrix} 0.2361 & 0 \\ 0 & -4.2361 \end{bmatrix}$$

3: Evaluate the Diagonal Matrix:

$$\begin{bmatrix} f_0() & 0 \\ 0 & f_0() \end{bmatrix}$$

4. Return back to the original basis to get the final answer:

$$f_0 \left(\begin{bmatrix} 1 & 2 \\ 2 & 3 \end{bmatrix} \right) = V \begin{bmatrix} \quad \\ \quad \end{bmatrix} V^\dagger$$

- So, to evaluate $[?] = f_0([H] - \mu[I])$

We simply take

$$V \begin{bmatrix} f_0(\mathbf{e}_1 - \mathbf{m}) & & \\ & f_0(\mathbf{e}_2 - \mathbf{m}) & \\ & & \ddots \end{bmatrix} V^\dagger$$

Real Space Density of a Matrix

10:20

- Summarizing, electron density in real space is given by $V f_0 (H_{\text{diag}} - \mu I) V^\dagger$
- Recall, V is structured as follows:

$$V = \begin{matrix} \xrightarrow{\text{eigenstates}} \\ \downarrow x_i \\ \left[\begin{array}{ccc} \dots & ||| & \dots \end{array} \right] \end{matrix}$$

where the eigenvectors are columns

- As well, the ordering of V and V^\dagger can be remembered through the mnemonic:

$$\left[\begin{array}{c} \xrightarrow{\text{new}} \\ \downarrow \text{old} \end{array} \right] \left[\begin{array}{c} \xrightarrow{\text{new}} \\ \downarrow \text{new} \end{array} \right] \left[\begin{array}{c} \xrightarrow{\text{old}} \\ \downarrow \text{new} \end{array} \right] = V H_{\text{diag}} V^\dagger$$

- Another common expression for the density matrix in real space is:

$$\mathbf{r}(x, x') = \sum_a \mathbf{f}_a(x) f_0(\mathbf{e}_a - \mathbf{m}) \mathbf{f}_a(x')$$

- Finally, for *any* basis remember that the diagonal elements of ? always give the electron density "n" in that basis

- What are the off diagonal elements for? Firstly, they are needed to transform to and from basis sets. Secondly, they are important for calculating observables (more on this later)

Physical Meaning of Electron Density

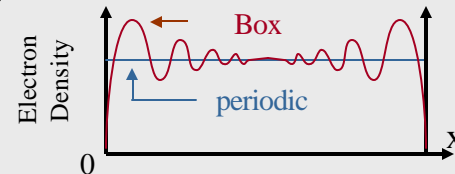
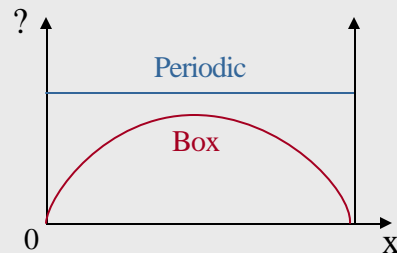
16:16

- Electron density can be used to analyze the characteristics of many systems
- For example, consider the wave functions of the periodic and infinite wall Boundary Conditions (B.C.)

- The electron densities of the periodic and infinite wall B.C.'s are identical at the center but differ at the ends

Electron Density in Periodic and infinite wall boundary Conditions

? with periodic and box B.C



- From this we see intuitively that boundary conditions can be ignored in large systems, since it is often what occurs far from the boundaries that we are interested in (i.e. solids)

Electron Density and "Wave Function"

18:28

- Recall, given a wave function f_a the probability distribution of this wave function is $|f_a|^2$

- Hypothetically, suppose we could write the wave function of a system as such that

$$\Psi = \sum_a f_a(x) \sqrt{f_a}$$

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

But this is not possible, since $\Psi^* \Psi$ produces cross terms

$$f_a^* f_b \sqrt{f_a f_b}$$

- The only way this could work is to write

$$\Psi = \sum_a f_a(x) C_a$$

And view C 's as stochastic numbers

Such that $\langle C_a C_b^* \rangle = 0, a \neq b$

And

$$\langle C_a C_b^* \rangle = f_a$$

- In a way, $C_a C_b^*$ is the density matrix in the eigenstate basis ($\rho_{a\beta} = f_a \delta_{a\beta}$)

- Why is it that P is diagonal only in the eigenstate basis?

• To answer this question, in part, begin by looking at the Schrödinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H_{op} \Psi \text{ or}$$

$$i\hbar \frac{\partial \Psi}{\partial t} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_n \end{bmatrix} = \begin{bmatrix} \mathbf{e}_1 & & & \\ & \mathbf{e}_2 & & \\ & & \ddots & \\ & & & \mathbf{e}_n \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_n \end{bmatrix}$$

which by separation of variables (time and space) gives n linearly independent equations

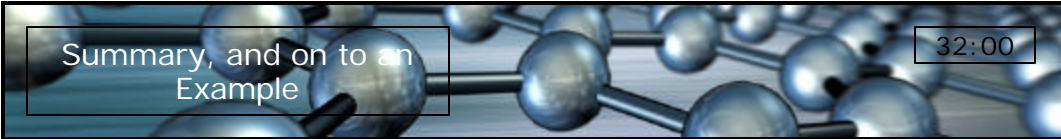
$$\text{• i.e. } i\hbar \frac{\partial \Psi_1}{\partial t} = \mathbf{e}_1 \Psi_1 \quad i\hbar \frac{\partial \Psi_2}{\partial t} = \mathbf{e}_2 \Psi_2$$

$$\dots i\hbar \frac{\partial \Psi_n}{\partial t} = \mathbf{e}_n \Psi_n \text{ and}$$

$$\Psi_j(t) = \Psi_j(0) e^{-i\mathbf{e}_j t / \hbar}$$

- Hence, there exists no overlap between members of the eigenstate basis; so the Hamiltonian must be diagonal

• From this one might intuitively infer that the density matrix must also be diagonal with the diagonal elements given by the appropriate Fermi function for the state that each eigenvalue represents. What isn't obvious, and will be explained later, is exactly why we use f_a and where it comes from.



Summary, and on to an Example

32:00

- Main Points:

- Fermi distribution used to write ρ in the eigenstate basis
- The general formulation for the **EQUILIBRIUM** density matrix, in any basis, is $\rho = f_0(H - \mu I)$
- Most properties of a material can be calculated from the density matrix

- *Example:* suppose you want to calculate current flow

$$I = (-q)nv,$$

where n is the electron density and v is the velocity. Given that n is known from the density matrix ρ , we must find v . To calculate v we must develop a velocity operator

Example: Current Flow

32:47

- The expectation value of a quantity, such as v , is

$$\langle v \rangle = \int d\vec{r} \Psi^* v_{op} \Psi$$

Back to devising v_{op} ... we know that the operator for momentum in one dimension is $p_{op} = -i\hbar \frac{\partial}{\partial x}$

or in general $\vec{p}_{op} = -i\hbar \nabla$

And, velocity is related to momentum by $p=mv$, thus

$$\vec{v} = -i\hbar / m \nabla$$

- Let us expand upon $\langle v \rangle$...

$$\begin{aligned} \langle v \rangle &= \int d\vec{r} \sum_a \mathbf{f}_a^*(\vec{r}) C_a^* v_{op} \\ &\quad \cdot \sum_b \mathbf{f}_b(\vec{r}) C_b = \sum_a \sum_b v_{ab} \mathbf{r}_{ab} \end{aligned}$$

where, in general, the matrix elements for any operator are

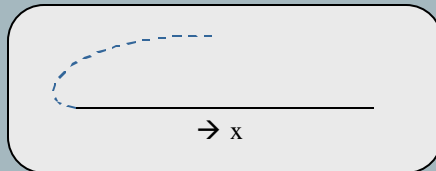
$$A_{ab} = \int d\vec{r} \mathbf{f}_a^* A_{op} \mathbf{f}_b$$

$$\therefore \langle v \rangle = \sum_a [\mathbf{v} \mathbf{r}]_{aa} = \text{Trace}(\mathbf{v} \mathbf{r})$$

Box with Periodic Boundary Conditions

40:52

- Consider a box with periodic boundary conditions
- Recall, such a box has the appearance



and the eigenvectors e^{+ikx} and e^{-ikx}

- Intuitively, the state e^{+ikx} can be said to possess positive momentum and carry current in the +x direction

- Likewise, the state e^{-ikx} carries current in the -x direction and has negative momentum
- So, the velocity matrix is

$$V = \begin{bmatrix} \frac{\hbar k}{m} & 0 \\ 0 & -\frac{\hbar k}{m} \end{bmatrix}$$

where $p_{op} = -i\hbar \frac{\partial}{\partial x}$

Given two electrons, at equilibrium each state is equally occupied ...

$$\mathbf{r} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$



Box with Periodic Boundary Conditions

45:30

- When voltage is applied, -positive terminal at the +x end- states move such that there is more current to the right and less to the left. i.e.

$$\mathbf{r} = \begin{bmatrix} 1.5 & 0 \\ 0 & 0.5 \end{bmatrix}$$

- However, interpreting ? becomes more difficult when working in another basis. For example, suppose instead of (e^{+ikx}, e^{-ikx}) we use $(\cos(kx), \sin(kx))$

- In this case the velocity matrix is

$$\mathbf{v} = \begin{bmatrix} \cos(kx) & \sin(kx) \\ 0 & i\hbar k / 2mL \\ -i\hbar k / 2mL & 0 \end{bmatrix} \text{ where } k = (2n\pi)/L$$

- Here it is not at all clear what the eigenvalues are, due to the off-diagonal nature of \mathbf{v} . To solve situations such as this, particularly on a much larger scale, the full machinery of QM must be employed.
- For this reason, we often take a semi-classical approach in large scale simulations. Meaning, we use orthogonal basis sets providing near diagonal operator matrices. This often makes results conceptually simpler to understand.