PH575 Spring 2014
Lecture \#28
Nanoscience: the case study of graphene and carbon nanotubes.


Nanoscience scale $\approx 1$-100 nm
"Artificial atoms"
Small size => discrete states
Large surface to volume ratio
Bottom-up vs. top-down construction



## A close look on single quantum dots <br> A. Zrenner <br> Walter Schottky Institut, Technische Universität München, D-85748 Garching, Germany

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Fig. 1. AFM images of self assembled $\mathrm{In}_{0.4} \mathrm{Ga}_{0.6} \mathrm{As}$ QDs grown by MBE on a GaAs substrate at a temperature of $530{ }^{\circ} \mathrm{C}$. Nominally 7.5 monolayers of $\mathrm{In}_{0.4} \mathrm{Ga}_{0.6} \mathrm{As}$, slightly above the critical thickness for Stranski-Krastanow growth have been deposited under the condition of nonrotated substrate. The resulting gradient in $\mathrm{In}_{0.4} \mathrm{Ga}_{0.6} \mathrm{As}$ coverage leads to a variation of the QD surface density across the wafer (upper part: $\sim 100 \mu \mathrm{~m}^{-2}$, lower part: $\sim 20 \mu \mathrm{~m}^{-2}$ ).

18, pp. 7790-7798, 8 May 2000


Fig. 2. Power dependent PL spectra from a single QD isolated by near field spectroscopy through a nano-aperture. At low excitation power $P L$ only the single exciton decay from the $s$-shell is observed (1X). At elevated $P L$ occupancies with two and more excitons are realized. The sequential biexciton decay leads to the appearance of the biexciton line (21) in the $p$-shell (2X). The decay of higher occupancies (for example 32,43) leads to new emission lines in the spectral regior of the $p$-shell and additional, further renormalized lines in the region of the $s$-shell

## Carbon nanotube



The measured vibration amplitude revealed an exceptionally high elastic Young's modulus of about $10^{12} \mathrm{~N} / \mathrm{m}^{2}$ (or one TPa) - about five times the value for steel.

This results in talk of a "space elevator", to tether an orbiter to earth



Graphene nanofabric. SEM micrograph of a strongly crumpled graphene sheet on a Si wafer. Note that it looks just like silk thrown over a surface. Lateral size of the image is 20 microns. Si wafer is at the bottom-right corner.


## GRAPHENE



Image "graphene molecule.jpg" is copyright of Chris Ewels (www.ewels.info)

Fig. 1. Phonon dispersion of graphene calculated within a valence force field (VFF) model (Aizawa).

armohair

There are two special cases: the armchair and the zig-zag CNT. The general case is called the chiral nanotube.

A CNT is made by cutting a strip of graphene so that the wrapping vector, shown in red at left, wraps around the circumference of the tube.


http://www.ewels.info/img/science/nanotubes/tube.angled.jpg

Various types of nanotubes

'zigzag'

'armchair'




Approximate 1-D band structure and density of states of (a) metallic CNT and (b) semiconducting CNT.

The band gap of a semiconducting tube is inversely proportional to its diameter $\mathrm{E}_{\mathrm{g}}=4 h v_{F} / 3 d$


Differential conductance of a CNT. Note how the conductance jumps every time the peak in the DoS lines up with the electron "supply reservoir"


Figure 2: LCAO-bandstructure of graphene.
$E\left(k_{x}, k_{y}\right)= \pm \gamma_{1} \sqrt{1+4 \cos \left(\frac{1}{2} k_{x} a_{0}\right) \cos \left(\frac{\sqrt{3}}{2} k_{y} a_{0}\right)+4 \cos ^{2}\left(\frac{k_{x} a_{0}}{2}\right)}$

The program
Identify unit cell and reciprocal lattice
Set up LCAO wavefunction
Set up Hamiltonian and Schrödinger' s equation
Project onto basis states
Set up coefficient matrix and solve eigenvalue determinant
Plot dispersion relation
Find Fermi energy
For nanotubes
Set up boundary constraints


The graphene lattice has 2 inequivalent C atoms per unit cell. Each one is bonded to 3 other C atoms in the plane via $s p^{2}$ hybrid orbitals, and each has one electron in a $p_{z}$ orbital perpendicular to the plane. The C-C bond distance is $1.421 \AA$.


$$
\begin{aligned}
& \vec{b}_{1}=\frac{2 \pi}{\sqrt{3} a_{0}}\left(1, \frac{1}{\sqrt{3}}\right) ;\left|\vec{b}_{1}\right|=\frac{4 \pi}{3 a_{0}} \\
& \vec{b}_{2}=\frac{2 \pi}{\sqrt{3} a_{0}}\left(-1, \frac{1}{\sqrt{3}}\right) ;\left|\vec{b}_{2}\right|=\frac{4 \pi}{3 a_{0}}
\end{aligned}
$$

The reciprocal lattice is triangular. The Wigner-Seitz cell (1st Brillouin zone) is shaded. There are 6 equivalent $K$ points (What are they?).

The program
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$$
\hat{H}\left|\Psi_{\vec{k}}\right\rangle=E(\vec{k})\left|\Psi_{\vec{k}}\right\rangle
$$

Set up LCAO wave function

$$
\left|\Psi_{\vec{k}}\right\rangle=\sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}|\phi(\vec{x}-\vec{R})\rangle
$$

2 atoms per unit cell

$$
|\phi(\vec{x})\rangle=b_{1}\left|\phi_{1}(\vec{x})\right\rangle+b_{2}\left|\phi_{2}(\vec{x})\right\rangle
$$

Hamiltonian

$$
\begin{aligned}
& \hat{H}=\frac{\hat{p}^{2}}{2 m}+\sum_{\vec{R}} V_{a t}\left(\vec{x}-\vec{x}_{1}-\vec{R}\right)+V_{a t}\left(\vec{x}-\vec{x}_{2}-\vec{R}\right) \\
& \hat{H}=\frac{\hat{p}^{2}}{2 m}+V_{a t}\left(\vec{x}-\vec{x}_{1}\right)+ \\
& V_{a t}\left(\vec{x}-\vec{x}_{2}\right)+\sum_{\vec{R} \neq 0} V_{a t}\left(\vec{x}-\vec{x}_{1}-\vec{R}\right)+V_{a t}\left(\vec{x}-\vec{x}_{2}-\vec{R}\right)
\end{aligned}
$$

$$
\begin{aligned}
\hat{H}\left|\phi_{1}(\vec{x})\right\rangle & =\left[\frac{\hat{p}^{2}}{2 m}+V_{a t}\left(\vec{x}-\vec{x}_{1}\right)\right]\left|\phi_{1}(\vec{x})\right\rangle \\
& +\left[V_{a t}\left(\vec{x}-\vec{x}_{2}\right)+\sum_{\vec{R} \neq 0} V_{a t}\left(\vec{x}-\vec{x}_{1}-\vec{R}\right)+V_{a t}\left(\vec{x}-\vec{x}_{2}-\vec{R}\right)\right]\left|\phi_{1}(\vec{x})\right\rangle \\
& =\varepsilon_{1}\left|\phi_{1}(\vec{x})\right\rangle+\left[V_{a t}\left(\vec{x}-\vec{x}_{2}\right)+\sum_{\vec{R} \neq 0} V_{a t}\left(\vec{x}-\vec{x}_{1}-\vec{R}\right)+V_{a t}\left(\vec{x}-\vec{x}_{2}-\vec{R}\right)\right]\left|\phi_{1}(\vec{x})\right\rangle \\
& =\varepsilon_{1}\left|\phi_{1}(\vec{x})\right\rangle+\Delta U_{1}\left|\phi_{1}(\vec{x})\right\rangle \\
\hat{H}\left|\phi_{2}(\vec{x})\right\rangle & =\varepsilon_{2}\left|\phi_{2}(\vec{x})\right\rangle+\Delta U_{2}\left|\phi_{2}(\vec{x})\right\rangle
\end{aligned}
$$

Onsite matrix element $\quad \varepsilon_{1}=\varepsilon_{2} \quad$ Set to zero by choice

$$
\hat{H}\left|\phi_{j}\right\rangle=\Delta U_{j}\left|\phi_{j}\right\rangle
$$

$\Delta U_{1(2)}$ Can be considered the "perturbing" potential for 1 (2)

The program
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Project onto basis states
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For nanotubes
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$$
\hat{H}\left|\Psi_{\vec{k}}\right\rangle=E(\vec{k})\left|\Psi_{\vec{k}}\right\rangle
$$

Now project onto basis states

$$
\begin{aligned}
& \left\langle\phi_{j}\right| \hat{H}\left|\Psi_{\vec{k}}\right\rangle=\left\langle\phi_{j}\right| E(\vec{k})\left|\Psi_{\vec{k}}\right\rangle \\
& \left\langle\phi_{j}\right| \Delta U_{j}\left|\Psi_{\vec{k}}\right\rangle=E(\vec{k})\left\langle\phi_{j} \mid \Psi_{\vec{k}}\right\rangle
\end{aligned}
$$

## Step 1

$\left\langle\phi_{j} \mid \Psi_{\vec{k}}\right\rangle$
$\left\langle\phi_{\mid} \mid \Psi_{\vec{k}}\right\rangle=\left\langle\phi_{\mid}\right| \sum_{R} e^{\overrightarrow{\vec{k}} \vec{k}}|\phi(\vec{x}-\vec{R})\rangle$
$\left\langle\phi_{1} \mid \Psi_{\bar{k}}\right\rangle=b_{1}+b_{2} \gamma_{0} \alpha(\vec{k})$


Step 2
$\left\langle\phi_{j}\right| \Delta U_{j}\left|\Psi_{\vec{k}}\right\rangle$
$\left\langle\phi_{1}\right| \Delta U_{1}\left|\Psi_{\bar{k}}\right\rangle=\left\langle\phi_{1}\right| \Delta U_{1} \sum_{R} e^{\vec{\pi} \vec{k}}|\phi(\vec{x}-\vec{R})\rangle$
$\left\langle\phi_{1}\right| \Delta U_{\|}\left|\Psi_{k}\right\rangle=b_{2} \gamma_{1} \alpha(\vec{k})$


$$
\left\langle\phi_{1} \mid \Psi_{\vec{k}}\right\rangle=\left\langle\phi_{1}\right| \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}|\phi(\vec{x}-\vec{R})\rangle
$$

$$
\left\langle\phi_{1} \mid \Psi_{\vec{k}}\right\rangle=b_{1}+b_{2} \gamma_{0} \alpha(\vec{k})
$$

$$
\begin{aligned}
& \text { Step } 1 \\
& =\left\langle\phi_{1} \mid \Psi_{\vec{k}}\right\rangle=\left\langle\phi_{1}\right| \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}|\phi(\vec{x}-\vec{R})\rangle \\
& =\left\langle\phi_{1}\right| \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}\left\{b_{1}\left|\phi_{1}(\vec{x}-\vec{R})\right\rangle+b_{2}\left|\phi_{2}(\vec{x}-\vec{R})\right\rangle\right\} \\
& =\underbrace{b_{1}\left\langle\phi_{1}(\vec{x}) \mid \phi_{1}(\vec{x})\right\rangle+b_{2}\left\langle\phi_{1}(\vec{x}) \mid \phi_{2}(\vec{x})\right\rangle}_{\vec{R}=0} \\
& +\underbrace{b_{1} e^{-i \vec{k} \cdot \vec{a}_{1}}\left\langle\phi_{1}(\vec{x}) \mid \phi_{1}\left(\vec{x}+\vec{a}_{1}\right)\right\rangle+b_{2} e^{-i \vec{k} \cdot \vec{a}_{1}}\left\langle\phi_{1}(\vec{x}) \mid \phi_{2}\left(\vec{x}+\vec{a}_{1}\right)\right\rangle}_{\vec{R}=-\vec{a}_{2}} \\
& +\underbrace{b_{1} e^{-i \vec{k} \cdot \vec{a}_{2}}\left\langle\phi_{1}(\vec{x}) \mid \phi_{1}\left(\vec{x}+\vec{a}_{2}\right)\right\rangle+b_{2} e^{-i \vec{k} \cdot \vec{a}_{2}}\left\langle\phi_{1}(\vec{x}) \mid \phi_{2}\left(\vec{x}+\vec{a}_{2}\right)\right\rangle}_{\vec{R}=-\vec{a}_{1}}
\end{aligned}
$$

$$
\begin{aligned}
& \left\langle\phi_{1} \mid \Psi_{\bar{k}}\right\rangle=b_{1} \\
& +b_{2}\left\langle\phi_{1}(\vec{x}) \mid \phi_{2}(\vec{x})\right\rangle \\
& +b_{2} e^{-\vec{k} \vec{k}_{1}}\left\langle\phi_{1}(\vec{x}) \mid \phi_{2}\left(\vec{x}+\vec{a}_{1}\right)\right\rangle \\
& +b_{2} e^{-i \vec{k} \vec{a}_{2}}\left\langle\phi_{1}(\vec{x}) \mid \phi_{2}\left(\vec{x}+\vec{a}_{2}\right)\right\rangle \\
& \left\langle\phi_{1} \mid \Psi_{\vec{k}}\right\rangle=b_{1}+b_{2} \gamma_{0}\left[1+e^{-i \vec{k} \bar{w}_{1}}+e^{-i \vec{k} \bar{k}_{2}}\right] \\
& \left\langle\phi_{1} \mid \Psi_{\vec{k}}\right\rangle=b_{1}+b_{2} \gamma_{0} \alpha(\vec{k}) \\
& \left\langle\phi_{2} \mid \Psi_{\vec{k}}\right\rangle=b_{2}+b_{1} \gamma_{0} \alpha^{*}(\vec{k})
\end{aligned}
$$

Step 2
$\left\langle\phi_{j}\right| \Delta U_{j}\left|\Psi_{\vec{k}}\right\rangle$

$$
\begin{aligned}
& \left\langle\phi_{1}\right| \Delta U_{1}\left|\Psi_{\vec{k}}\right\rangle=\left\langle\phi_{1}\right| \Delta U_{1} \sum_{\vec{R}} e^{\vec{k} \vec{k} \vec{k}}|\phi(\vec{x}-\vec{R})\rangle \\
& \left\langle\phi_{1}\right| \Delta U_{1}\left|\Psi_{\vec{k}}\right\rangle=b_{2} \gamma_{1} \alpha(\vec{k})
\end{aligned}
$$

## Step 2

## $\left\langle\phi_{j}\right| \Delta U_{j}\left|\Psi_{\vec{k}}\right\rangle$

$$
\begin{aligned}
& \left\langle\phi_{1}\right| \Delta U_{1}\left|\Psi_{\vec{k}}\right\rangle=\left\langle\phi_{1}\right| \Delta U_{1} \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}|\phi(\vec{x}-\vec{R})\rangle \\
& =\left\langle\phi_{1}\right| \Delta U_{1} \sum_{\vec{R}} e^{i \vec{k} \cdot \vec{R}}\left\{b_{1}\left|\phi_{1}(\vec{x}-\vec{R})\right\rangle+b_{2}\left|\phi_{2}(\vec{x}-\vec{R})\right\rangle\right\} \\
& =\underbrace{b_{1}\left\langle\phi_{1}(\vec{x})\right| \Delta U_{1}\left|\phi_{1}(\vec{x})\right\rangle+b_{2}\left\langle\phi_{1}(\vec{x})\right| \Delta U_{1}\left|\phi_{2}(\vec{x})\right\rangle}_{\vec{R}=0}
\end{aligned}
$$

$$
+\underbrace{b_{1} e^{-i \vec{k} \cdot \vec{a}_{1}}\left\langle\phi_{1}(\vec{x})\right| \Delta U_{1}\left|\phi_{1}\left(\vec{x}+\vec{a}_{1}\right)\right\rangle+b_{2} e^{-i \vec{k} \cdot \vec{a}_{1}}\left\langle\phi_{1}(\vec{x})\right| \Delta U_{1}\left|\phi_{2}\left(\vec{x}+\vec{a}_{1}\right)\right\rangle}_{\vec{R}=-\vec{a}_{1}}
$$

$$
+\underbrace{b_{1} e^{-i \vec{k} \cdot \vec{a}_{2}}\left\langle\phi_{1}(\vec{x})\right| \Delta U_{1}\left|\phi_{1}\left(\vec{x}+\vec{a}_{2}\right)\right\rangle+b_{2} e^{-i \vec{k} \cdot \vec{a}_{2}}\left\langle\phi_{1}(\vec{x})\right| \Delta U_{1}\left|\phi_{2}\left(\vec{x}+\vec{a}_{2}\right)\right\rangle}_{\vec{R}=-\vec{a}_{2}}
$$

Define hopping (offsite) matrix element

$$
\begin{gathered}
\gamma_{1}=\left\langle\phi_{1}\right| \Delta U_{1}\left|\phi_{2}\right\rangle=\left\langle\phi_{2}\right| \Delta U_{2}\left|\phi_{1}\right\rangle \\
\left\langle\phi_{1}\right| \Delta U_{1}\left|\Psi_{\vec{k}}\right\rangle=b_{2} \gamma_{1}\left[1+e^{-i \vec{k} \cdot \vec{u}_{1}}+e^{-i \vec{k} \cdot \vec{a}_{2}}\right]=b_{2} \gamma_{1} \alpha(\vec{k}) \\
\left\langle\phi_{2}\right| \Delta U_{2}\left|\Psi_{\vec{k}}\right\rangle=b_{1} \gamma_{1}\left[1+e^{+i \vec{k} \cdot \vec{a}_{1}}+e^{+i \vec{k} \cdot \vec{a}_{2}}\right]=b_{1} \gamma_{1} \alpha^{*}(\vec{k})
\end{gathered}
$$

## End step 2

Now remember these were the equations we began with:

$$
\left\langle\phi_{j}\right| \Delta U_{j}\left|\Psi_{\vec{k}}\right\rangle=E(\vec{k})\left\langle\phi_{j} \mid \Psi_{\vec{k}}\right\rangle
$$

The program
$\checkmark$ Identify unit cell and reciprocal lattice
$\checkmark$ Set up LCAO wavefunction
$\checkmark$ Set up Hamiltonian and Schrödinger's equation
$\checkmark$ Project onto basis states
Set up coefficient matrix and solve eigenvalue determinant
Plot dispersion relation
Find Fermi energy
For nanotubes
Set up boundary constraints

Now remember these were the equations we began with:

$$
\left\langle\phi_{j}\right| \Delta U_{j}\left|\Psi_{\vec{k}}\right\rangle=E(\vec{k})\left\langle\phi_{j} \mid \Psi_{\vec{k}}\right\rangle
$$

And we found in step 2 and step 1 that:
$\left\langle\phi_{1}\right| \Delta U_{1}\left|\Psi_{\vec{k}}\right\rangle=b_{2} \gamma_{1} \alpha(\vec{k})$
$\left\langle\phi_{1} \mid \Psi_{\vec{k}}\right\rangle=b_{1}+b_{2} \gamma_{0} \alpha(\vec{k})$
$\left\langle\phi_{2}\right| \Delta U_{2}\left|\Psi_{\vec{k}}\right\rangle=b_{1} \gamma_{1} \alpha^{*}(\vec{k})$
$\left\langle\phi_{2} \mid \Psi_{\vec{k}}\right\rangle=b_{2}+b_{1} \gamma_{0} \alpha^{*}(\vec{k})$

It's easy to put these together to get the eigenvalue equation:

$$
\left|\begin{array}{cc}
E(\vec{k}) & \alpha\left(\gamma_{0} E(\vec{k})-\gamma_{1}\right) \\
\alpha *\left(\gamma_{0} E(\vec{k})-\gamma_{1}\right) & E(\vec{k})
\end{array}\right|=0
$$

The solution, in the limit of small $\gamma_{0}$ is

$$
E(\vec{k})^{2}=\gamma_{1}^{2}|\alpha(\vec{k})|^{2} \Rightarrow E(\vec{k})= \pm \gamma_{1}|\alpha(\vec{k})|
$$

Recall the definition of $\alpha(k)$ :

$$
\alpha(\vec{k})=\left[1+e^{-i \vec{k} \cdot \vec{a}_{1}}+e^{-i \vec{k} \cdot \vec{a}_{2}}\right]
$$

You find $|\alpha(k)|$ and show that

$$
E(\vec{k})= \pm \gamma_{1} \sqrt{3+2 \cos \left(\vec{k} \cdot \vec{a}_{1}\right)+2 \cos \left(\vec{k} \cdot \vec{a}_{2}\right)+2 \cos \left(\vec{k} \cdot\left[\vec{a}_{2}-\vec{a}_{1}\right]\right)}
$$

And explicitly in terms of $x$ and $y$ coordinates ...

$$
E\left(k_{x}, k_{y}\right)= \pm \gamma_{1} \sqrt{1+4 \cos \left(\frac{\sqrt{3}}{2} k_{x} a_{0}\right) \cos \left(\frac{3}{2} k_{y} a_{0}\right)+4 \cos ^{2}\left(\frac{\sqrt{3} k_{x} a_{0}}{2}\right)}
$$

The program
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The dispersion relation for graphene!


Figure 2: LCAO-bandstructure of graphene.

Where is the Fermi energy? Notice the $K$ points. What is $E\left(K_{x}, K_{y}\right)$ ?


$$
E\left(k_{x}, k_{y}\right)= \pm \gamma_{1} \sqrt{2+4 \cos \left(\frac{\sqrt{3}}{2} k_{x} a_{0}\right) \cos \left(\frac{3}{2} k_{y} a_{0}\right)+2 \cos ^{2}\left(\frac{\sqrt{3}}{2} k_{x} a_{0}\right)}
$$

New feature for nanotubes is that boundary constraints are important.
The wave vector parallel to the axis of the tube in unconstrained (for practical purposes)
The wave vector perpendicular to the axis must result in a wavelength that "fits" into the circumference.

Armchair:

$$
\begin{gathered}
\vec{w}=N\left(\vec{a}_{1}+\vec{a}_{2}\right) \\
\sqrt{3} N a=m \lambda_{m} \Rightarrow k_{y, m}=m \frac{2 \pi}{\sqrt{3} N a}
\end{gathered}
$$

Various types of nanotubes

‘zigzag'
'armchair'


$$
\sqrt{3} N a=m \lambda_{m} \Rightarrow k_{y, m}=m \frac{2 \pi}{\sqrt{3} N a}
$$



Figure 6: Shown is the 1. Brillouin zone in reciprocal space. The lines are the allowed (and independent) $\vec{k}$ giving rise to the 1d-bandstructure of a $(10,10)$ armchair carbon nanotube.

$$
E\left(k_{x}, k_{y}\right)= \pm \gamma_{1} \sqrt{1+4 \cos \left(\frac{1}{2} k_{x} a\right) \cos \left(\frac{\sqrt{3}}{2} k_{y} a\right)+4 \cos ^{2}\left(\frac{k_{x} a}{2}\right)}
$$

Figure 5: Bandstructure of a $(10,10)$ armchair carbon nanotube. The shaded region is the 1 . Brillouin zone. Note, each band is doubly degenerate, except for the ones crossing $E=0$ and the ones with maximal and minimal energy. There are in total 40 bands.


## Armchair CNTs are metallic



## Zig-zag CNTs are metallic or semiconducting

General wrapping vector (but limited to vicinity of the Fermi energy):

$$
E\left(k_{\|}\right)= \pm \frac{2 \hbar v_{F}}{d} \sqrt{\left(\frac{m-n}{3}+p\right)^{2}+\left(\frac{k_{\|} d}{2}\right)^{2}} \quad \vec{w}=n \vec{a}_{1}+m \vec{a}_{2}
$$



Metallic; $m-n$ is a multiple of 3

Semiconducting; $m-n$ is NOT a multiple of 3

