DEFECTS IN 2D MATERIALS:
HOW WE TAUGHT ELECTRONIC SCREENING TO MACHINES

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Theory and simulation of materials: focus on electronic excitations
DEFECT ENGINEERING

PN-junction: building block of semiconductor technology

Defects play a key role:

- donate electrons or holes to host material
- formation of charged ions
- charged defects scatter electrons
Promise of ultrathin devices with novel functionality

field effect transistor based on 2d semiconductor MoS$_2$

gas sensor based on graphene
Example: adsorbed atom
CHARGED DEFECTS IN 2D MATERIALS

\[
V_{scr}(r) = \int dr' \epsilon^{-1}(r, r') V_{bare}(r')
\]

\[
= V_{bare} + \int dr' \frac{n_{ind}(r')}{|r - r'|}
\]
THEORETICAL DESCRIPTION

Challenges:
• screened potential has complicated spatial dependence
• screening in 2D is weaker than in 3D
  ▶ large supercells
• charge transfer is difficult to compute
EXPERIMENTAL STUDY OF CHARGED DEFECTS

Scanning tunneling spectroscopy (STS):
- add or remove electrons from sample
- probe quasiparticle excitations
- experiments in Crommie group (Berkeley)
SINGLE ADATOM ON GRAPHENE

STM image of single calcium atom on graphene

electrons tunnel from graphene to tip


single adatom influences thousands of graphene atoms
DOPING DEPENDENCE

Effect of changing the graphene electron concentration via gate voltage $V_g$

For tip voltage such that electron tunnel from tip to graphene:

Modelling charged adsorbates on doped graphene:
- use tight-binding to model supercells with 100,000 carbon atoms
- charge transfer $Z = 0.7|e|$ from experimental measurement of Fermi level shift
- screened potential: random phase approximation
- calculate local density of states (LDOS)

\[
\epsilon(q) = \begin{cases} 
\epsilon_s + \frac{2\pi e^2 \text{DOS}(E_F)}{q}, & q \leq 2k_F, \\
\epsilon_s + \frac{2\pi e^2 \text{DOS}(E_F)}{q} \left[1 - \frac{1}{2} \sqrt{1 - \left(\frac{2k_F}{q}\right)^2} + \frac{q}{4k_F} \cos^{-1} \frac{2k_F}{q}\right], & q > 2k_F,
\end{cases}
\]
THEORY RESULTS

STS images for tunneling from graphene to tip:

THEORY RESULTS

STS images for tunneling from tip to graphene:

(a) $V_g = 0$ V
(b) $V_g = -30$ V
(c) $V_g = -60$ V
(d) p-doped experiment:
   - 0.15 eV above Dirac point
   - $V_g = 0$ V
   - $V_g = -5$ V
   - $V_g = -10$ V
   - $V_g = -15$ V
   - $V_g = -20$ V
   - $V_g = -30$ V
   - $V_g = -45$ V
   - $V_g = -60$ V

(e) p-doped theory:
   - 0.15 eV above Dirac point
   - $n = 3.0 \times 10^{11}$ cm$^{-2}$
   - $n = 4.9 \times 10^{11}$ cm$^{-2}$
   - $n = 6.1 \times 10^{11}$ cm$^{-2}$
   - $n = 1.0 \times 10^{12}$ cm$^{-2}$
   - $n = 1.2 \times 10^{12}$ cm$^{-2}$
   - $n = 1.8 \times 10^{12}$ cm$^{-2}$
   - $n = 2.4 \times 10^{12}$ cm$^{-2}$
   - $n = 3.5 \times 10^{12}$ cm$^{-2}$

BAND BENDING

Electric potential shifts the energies of electronic states

p-type  n-type

hole  electron

depletion layer

-  +  -  +  -  +

electric field

E_C  E_F

E_V

Electric potential shifts the energies of electronic states

BAND BENDING

LDOS

w/o Ca

w/o Ca

Electric potential shifts the energies of electronic states.
Electric potential shifts the energies of electronic states
OPEN QUESTIONS

• How to calculate the charge transfer?
• Is screening model ok? Need nonlinear response?

In principle: these questions can be answered by DFT calculations

But: DFT calculations for 100,000 atoms are … uncomfortable
使用 DFT 来计算简单/小系统的 $E\{R\}$ 的能量。使用训练集来确定更简单模型/算法（例如神经网络）的参数。使用更简单模型来对复杂/大系统的分子动力学进行模拟。
MULTISCALE APPROACH FOR CHARGED DEFECTS

DFT in small supercell

- calculate screened potential (training set)

Parametrize model in small supercell

- use non-atomistic model for graphene
- point charge for defect
- $Z$ and $E_F$ are fitting parameters

Use model potential in tight-binding

Evaluate model in large supercell

continuum model
Non-linear Thomas-Fermi (NLTF) approach:

\[
V_{\text{scr}}^{\text{cont}}(r; \mu) = Zv_{\text{imp}}(r) + \int d^2 r'[n(r') - n_0]v_0(r - r'),
\]

where \( n_0(\mu) = \mu|\mu|/(\pi v_F^2) \) and \( n(r) = n_0(\mu - V_{\text{scr}}(r)) \)

- Thomas-Fermi approach only captures intraband transitions
- include interband transition in linear response (via dielectric matrix)
RESULTS

Parametrization of continuum model using ab initio screened potential

Fitness metric $F$ as function of model parameter $E_F$ and $Z$

Corsetti, Mostofi, JL, 2D Materials (2017)
RESULTS

Parametrization of continuum model using ab initio screened potential

Optimal parameters for defect charge $Z$:

<table>
<thead>
<tr>
<th>Model</th>
<th>$Z$ (e)</th>
<th>$\mathcal{F}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTF</td>
<td>0.3</td>
<td>$8.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>LTF + inter</td>
<td>1.3</td>
<td>$8.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>NLTF</td>
<td>1.6</td>
<td>$9.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>NLTF + inter</td>
<td>1.6</td>
<td>$7.4 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

- all theories have similar fitness, but different parameters
- nonlinearity and interband transitions are important
- But: **only manifest themselves as rescaling of screening potential**

Impurity states of charged defects in MoS$_2$

- tight-binding calculations with 8,000 atoms
- screened potential from ab initio RPA calculation
- defect charge is parameter

Most strongly bound defect states for $Z=-0.25$ |e| (=acceptor defect):

Increasing binding energy
Comparison to 2d hydrogen model:

- impurity states similar to 2d hydrogen model
- But why multiple 1s states?

Aghajanian, Mostofi, JL, Scientific Reports (2018)
Phosphorus substitutional in silicon crystal:

- phosphorus has one more valence electron than silicon
- extra electron forms 3D hydrogenic state with positive core
- But: replace electron mass by effective mass from band structure
- And: reduce attractive Coulomb interaction by dielectric constant

Binding energy:

$$\epsilon = \frac{m^*}{m} \frac{1}{\epsilon^2} \times 13.6 \text{ eV}.$$
Band structure of MoS$_2$:

- Valence band has multiple maxima: K, K', Gamma
- Each maximum acts as 2d hydrogen atom and contributes series of states

Aghajanian, Mostofi, JL, Scientific Reports (2018)
CHARGED DEFECTS IN 2D SEMICONDUCTORS

Binding energy as function of impurity charge $Z$:

- small $|Z|$: $1s$ state from K/K' (=VBM) more strongly bound
- larger $|Z|$: binding energy of $1s$ state at Gamma increases quickly due to large $m^*$
- crossover at critical $|Z| = 0.35$

Similar results with Keldysh model for screened potential (dashed lines)
CHARGED DEFECTS IN 2D SEMICONDUCTORS

Donor atoms:

- weak spin-orbit coupling in conduction band
- $1s$ states from $K$ and $K'$ can hybridize:
  \[
  \Psi_\pm = \frac{1}{\sqrt{2}} (\Psi_{1s,K} \pm \Psi_{1s,K'})
  \]
- splitting of hybridized states not captured by Keldysh model
- crossover from $K/K'$ state to state from $Q$ near $|Z|=0.6$
Strong electron correlations in two dimensions

Experimental observations (Cao et al.):

- at a magic twist angle of 1.1 degree, TBG becomes insulator at quarter filling
- at T=1.7 K, TBG becomes superconductor
- similar phase diagram to cuprates
TWISTED BILAYER GRAPHENE

Theory: effective hopping model (Fu group, MIT) + renormalization group

\[ H = -t \sum_{\langle i,j \rangle} \sum_{\sigma=\uparrow,\downarrow} \left( c_{i,\sigma,p}^\dagger c_{j,\sigma,p} + H.c. \right) + U \sum_{i} n_{i}n_{i}, \]

phase diagram

flat bands near magic angle

Summary:
• understanding of charged defects in 2d materials is required for new devices
• modelling defects is challenging due to multiscale behaviour
• combining ab initio DFT with simpler models allows accurate description
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CHARGED DEFECTS IN 2D MATERIALS

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