Materials for Energy Conversion and Storage: 
*First-principles* Theory and Simulations

*Umesh V Waghmare*

Materials Theory Group

Theoretical Sciences Unit

J Nehru Centre for Advanced Scientific Research
Jakkur PO, Bangalore 560 064 INDIA

http://www.jncasr.ac.in/waghmare

waghmare@jncasr.ac.in

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Collaborators

Sharmila Shirodkar
Anjali Singh
Himanshu Chakraborty
Shashwat Anand
Krishna Mohan
Aseem Kshirsagar (IISER-P)

Sinthika and R Thapa, SRM University

Timothy Fisher (Purdue)  Ricardo Grau-Crespo (UC, London/Reading)

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Introduction & Methodology
Materials exhibit a remarkable diversity in properties that have been key to technological revolutions.

The origin of diversity in the World of Materials:
1. Chemical constituents: which elements or atoms?
2. Structure of a material: how are the atoms and their electrons organized in space-time?

Materials: *Key enablers* to technologies
Introduction: Energy

Energy Source: Solar, Wind, Tidal, Nuclear

Fuel: Chemical energy
Battery: Electro-chemical energy

Electricity

Work: Rearrangement of matter

Heat ~40%

How atoms interact with each other and with external fields?

Energy & storage involve Materials

Rearrangement of Atoms and Electrons! ↔ potential energy

McIntyre et al Nat Mat (2015)
Simulations should capture chemistry and structure

1. **Silicon vs Carbon**: both have 4 valence electrons
   - Si: great semiconductor, ground state
   - C: super-hard material, insulator
   Not ground state (difficult to synthesize!)

2. **Carbon**: Different Structures
   - **Graphene**: Zero band-gap semiconductor
   - **Nano-tubes**: Metallic and semiconducting
   - **Graphite**: In-plane conductor
   - **Fullerene**
Method of Simulations to design/explore a new material should:
1. Be applicable to wide range of compounds
2. Have a Parameter-free model [minimal dependence on experiments]
3. Capture material-specific properties: structure and chemistry: *e.g. Carbon vs Si*
4. Be efficient: cost should scale favorably with length and time-scales

How atoms interact with each other via electrons?
First-principles Theoretical Description of a Material

A Material = Collection of nuclei and electrons that interact via electro-magnetic fields

Nuclear motion: Newton’s laws
Electronic motion: Wave Mechanics

Lighter, faster electrons: Quantum ground state

Given atomic positions, Electrons distribute to minimize “total energy”: $E_t$

Electronic Structure!

Total Energy of Electrons and Nuclei: Inter-atomic Interaction Potential

Electrons--glue

Density Functional Theory, W Kohn et al; Nobel 1998
First-principles Theoretical Approach: **Total Energy Function**

*Chemistry:*

\[ Z_i: \text{Atomic numbers of atoms in a given material} \]

*Structure:*

\[ R_i: \text{Atomic positions of atoms in a given material} \]

\[
E_{tot}(Z_I, R_I) = E_{el}^G(Z_I, R_I) + E_{Coulomb}^{ion}(Z_I, R_I)
\]

**Quantum Mechanics**

- Inter-atomic potential \( T=0 K \)
- Hamiltonian of a collection of atoms

**Electrostatic Energy**

- Minimum energy quantum state of electrons: *Density Functional Theory, W Kohn et al*

**Free Energy**

- \( T > 0 K \)
- MD Monte Carlo
1. $E_t$ is the interatomic interaction potential: function of atomic positions [structure] and numbers [chemistry]!
2. Atomic positions that minimize $E_t$: Structure at $T=0K$
3. Derivatives of $E_t$ ↔ Properties of a material
**Materials Discovery & Design: Exciting science & Engineering**

**Experiments:**

- Highly Sophisticated
- Increasing resolution in time and space
- Expensive: consumables, instruments, humans
- However, essential!

**Materials:** too many combinatorial possibilities
- composition, structure, stability, ...

**Theory and Simulations:**

- Highly Sophisticated
- Increasing resolution in time and space
- Inexpensive: computers and algorithms

→ Reduce the number of possibilities for Experiments!
→ Predict New materials/structures, correct experiments
Many computer programs to do first-principles simulations are free, for example:

Quantum Espresso
http://www.pwscf.org

ABINIT
http://www.abinit.org

SIESTA
http://departments.icmab.es/leem/siesta

Many problems can be tackled with moderate computing resources
Three levels of structure of a Material obtained from *first-principles* simulations
Structure of a Solid: Atomic or Geometric

How atoms are organized in space

Coordination:
- Tetrahedral
- Octahedral,
- ...

Symmetry:
Restrictions on properties
- e.g. periodicity:
  translational symmetry & rigidity of crystals

Experiment: X-Ray Diffraction

Theory: Minimization of [free] Energy

Can Predict!
Structure of a Solid: Dynamical (phonons)

How atoms are organized or **oscillate** in time

1. **How stiff** is the solid? How fast does sound propagate?
2. Raman, IR spectroscopies: *Finger-print of a material*
3. **Thermodynamic Stability** of the Atomic Structure

Experiment: Inelastic Neutron Scattering

**Theory:** Derivatives of [free] Energy

*Can Predict!*
Structure of a Solid: Electronic

How Electron ‘Waves’ are organized in Space and Energy

Conduction Band

Band Gap

Valence Band

Bonds

Bands:
Highways/Channels Of “free”
Electronic Motion

Experiment: Spectroscopies

Theory: Direct Output [DFT]
Solar Energy

1. PhotoCatalytic
2. Photovoltaic solar cell
3. Electro-catalysis
4. Themoelectric
5. Fuel Cells
6. Na, Mg Batteries

Hydrogen: A clean fuel

Splitting of H₂O

Fossil Fuels

Engines, Automobiles

Wasted Heat

From Electronic Structure to Electrochemistry
Small band-gap is desirable: absorb a wide range of solar spectrum!

However,
1. higher energy electrons often lose energy to phonons: heat
2. water splitting requires e-hole at specific energy

Optimization of solar energy harnessing needs: engineering of both electrons and phonons
Solar Energy Harvesting: Photocatalysis

- **Band gap (Eg)** > 1.23 eV
- Conduction band > Red H₂O → **HER** Reduction: 4H⁺ + 4e → 2H₂
- Valence band < Ox H₂O → **OER** Oxidation: 2H₂O + 4h⁺ → O₂ + 4H⁺

http://payneresearch.org/research/photo-electrochemical-pec-water-splitting/
Photocatalysts

Conventional semiconductor photocatalysts: $\text{TiO}_2$, ZnO, CdS

Carbon based photocatalysts facilitate:
- Improved electron transport
- Increased light absorption
- Improves photocatalytic dispersion

Engineering $C_{2n}B_{M-n}N_{M-n}$ for Photocatalysis

*C*-substituted h-BN
Why C/BN?

Graphene:
2D hexagonal array of C atoms
Electronic bandgap = 0

White Graphene:
2D hexagonal boron nitride (BN)
Electronic bandgap > 5 eV

50 shades of grey Graphene!

Stacking heterostructures
Supporting/insulating graphene

In-plane heterostructures
Atom-thick circuitry
Levendorf et al. Nature 2012

2D alloys
Band gap control for optoelectronics
Lu et al. Nature Commun. 2013
Model

$n$ C/B and $n$ C/N substitutions in 3x3 supercell of h-BN ($n=0, 1, 2, 3$)

All symmetrically different configurations considered!
Taking advantage of the supercell symmetry using the SOD code

$C_{2x}(BN)_{1-x}$ bandgap

Control via composition and configuration!

SN Shirodkar, UV Waghmare, TS Fisher, R Grau-Crespo,
_PCCP_ 2015, 17, 13547-13552
$\text{C}_4\text{B}_7\text{N}_7$ (n= 2, M= 9)

- C dimerization in all favourable configurations and cohesive energy $\approx 0.23$ eV/fu
- Increase in doping $\rightarrow$ CB nearer to Red H$_2$O
Explaining increase of bandgap with C aggregation

Density of electronic states
Charge density of band edges
Energies of band edges

What is the effect of further increase in doping?
Band edge positions at higher C concentrations

- Lower band-gap, better CB & VB
- But more non-dimer configurations

C-substituted h-BN is not great for PEC
Can deviation from the stoichiometry $C_{1-x} (BN)_x$ help?

Carbon nitride and N-doped graphene:


-Electrocatalysis
Outstanding Electrochemical HER Performance of BC$_7$N$_2$

N, Carbon-rich BC$_7$N$_2$ \rightarrow \text{Excellent performance in expt}
Alignment of VB and CV wrt HER

1. Shifts VB and CB optimally to HER potential
2. Populates CB with large concentration of e: helps in HER

Excess N helps!

Descriptors of

*Site-specific* Catalytic Activity of

B and N substituted Graphene

Catalysis of Oxygen Reduction Reaction
Fuel Cells

Generate Electricity from a fuel (e.g. Hydrogen)

Oxygen Reduction Reaction

$$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O$$

at the Cathode (Pt)

Need for a material to replace Pt catalyst
## Descriptors of Catalytic Activity

<table>
<thead>
<tr>
<th>Descriptor</th>
<th>Class of catalyst</th>
<th>Calculation</th>
<th>Reaction</th>
<th>Optimal Catalyst(s) identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-band center</td>
<td>Transition Metals, Transition metal alloys</td>
<td>( \int_{-\infty}^{0} \rho_{d} EdE ) ( \int_{-\infty}^{0} \rho_{d} dE )</td>
<td>ORR</td>
<td>a) Pt and Pd have the smallest overpotentials among transition metals(^{21}). b) Pt(_3)Ni is a good alloying strategy(^{22})</td>
</tr>
<tr>
<td>( e_g ) Occupancy(^{23})</td>
<td>Transition metal oxides</td>
<td>( \int_{-\infty}^{0} \rho_{e_g} dE )</td>
<td>ORR</td>
<td>LaCoO(<em>3) ((t</em>{2g}^2e_g^1)) and LaNiO(<em>3) ((t</em>{2g}^6e_g^1))</td>
</tr>
<tr>
<td>( t_{2g} ) Occupancy(^{24})</td>
<td>Transition metal oxides</td>
<td>( \int_{-\infty}^{0} \rho_{t_{2g}} dE )</td>
<td>Oxygen Evolution Reaction (OER)</td>
<td>CuCoO(_2), PtCoO(_2)</td>
</tr>
<tr>
<td>O p-band center</td>
<td>Transition metal oxides</td>
<td>( \int_{-\infty}^{0} \rho_{p} EdE ) ( \int_{-\infty}^{0} \rho_{p} dE )</td>
<td>OER</td>
<td>((\text{Pr}<em>{0.5}\text{Ba}</em>{0.5})\text{CoO}_3)</td>
</tr>
<tr>
<td>( E_{\text{vac}, \text{Vacancy Formation Energy}} )</td>
<td>Core shell transition metal nanoparticles</td>
<td>( E_{\text{vac}} = E_{\text{vac, clean}} - \left(\frac{E_{\text{total}}^N}{N} + E_{\text{Atom}}^{N-1}\right) )</td>
<td>ORR</td>
<td>Pd(_3)Cu(_1)@Pt (core@shell)</td>
</tr>
<tr>
<td>( E_{\text{surf}, \text{Surface Energy}} )</td>
<td>Pure metals</td>
<td>( E_{\text{surf}} = \frac{1}{2A_n} \left( E_{\text{slab}} - NE_{\text{bulk}} \right) )</td>
<td>Hydrogen Evolution Reaction</td>
<td>Pt</td>
</tr>
</tbody>
</table>

*Noskov et al*

Electronic states near \( E_F \) or Gap

Sinthika, Waghmare and Thapa (2017)

**Descriptors:**
- Easy to calculate
- Correlate with Activity
Various Substitutional Sites of $C_{1-x}(\text{BN})_x$ for Catalysis

At $e_F$, $p_z$ orbital states are prominent: $\pi$ Electronic Structure
Descriptors of ORR Activity of Sites of $C_{1-x}(BN)_x$

$D_{pz}(E_F)$ and $O_{pz} = \left[\int_{-\infty}^{0} \rho_{pz} dE\right]_{\text{active site}} - \left[\int_{-\infty}^{0} \rho_{pz} dE\right]_{\text{carbon atom in pristine graphene}}$

Relevant Free Energy

$\Delta G_{OH} = (G_{OH(\text{grap})}) - (G(\text{grap}) + G_{OH^-})$

$\Delta G_{OH}$ is the "Key Performance Index"
A single **LOCAL** Electronic Descriptor of $C_{1-x}(BN)_x$

$$f(p_{Z-B}) = 2.95(O_{p_Z}) + D_{p_Z}(E_F)$$

---

Knowledge of projected density of electronic states:
Site-specific catalytic activity towards ORR
Structural Descriptors of ORR activity of $C_{1-x}(BN)_x$

Predictive Model:

$$\Delta G_{\text{OH-generated}}(N) = 1.09 - 0.13n_M - 0.33n_P - 0.68n_O$$

Easy to use, generalize to other $\pi$–bonded 2-D materials
Most Optimal Site $C_{1-x}(BN)_x$ for ORR

3N-para site: lowest over-potential of 0.48 eV

Sinthika, Waghmare and Thapa, in review, Small (2017)
Prediction of a new 2-D material: Photo-voltaic and photo-catalytic properties
Prediction of a New 2-D Material: \textit{NbN}

Two-Dimensional Rectangular and Honeycomb Lattices of NbN: Emergence of Piezoelectric and Photocatalytic Properties at Nanoscale

Shashwat Anand, Krishnamohan Thekkepat, and Umesh V. Waghmare*

Nano Letters 16, 126 (2016)
Theoretical Predictions on 2D NbN

2D Piezoelectric
2.06 eV/NbN

Rocksalt NbN (CN = 6)
Superconductor ($T_C = 16$ K)

Thinnest Superconductor ($T_C > 4$ K)
1.35 eV/NbN

h-NbN (CN = 3)
Novel Structures of a Known Compound

s-NbN (CN = 4)
Electronic Structure

h-NbN: Semiconductor:

- h-NbN: Semiconductor (like MoS$_2$)

Optical Properties

- Exciton Binding $E = 0.12$ eV

- Good absorption
- VB and CB: Bracket HER, OER

Great for photo-catalytic splitting of water
Dynamical Structure of 2D NbN: Applications

High Energy Photo Electrons lose energy to optic phonons, which can not decay into acoustic modes readily.

Applications in
Hot carrier solar cells
Solar Splitting of H₂O

Energy Storage is a Big Challenge
Energy Storage: *Batteries*

- **Energy Storage**: critical due to intermittency of renewable energy sources
- **2-D Carbon-based materials**: promise as anodes in Li-ion batteries
- Li ion batteries: saturating in energy capacity
- **Na and Mg ion batteries**: earth abundant and attractive
- Mg-batteries: high gravimetric energy density and high voltage
- Challenges for Mg batteries:
  1. Stability of an electrolyte against reduction by Mg
  2. Need for a cathode with high voltage and fast kinetics of Mg$^{2+}$
2D Materials for a Cathode in Mg$^{2+}$ Batteries

MXenes: $M_{N+1}X_NT_x$ ($M$: Transition Metal; $X$: C or N; $T$: O, F or OH)

Expected to give high voltage, but slow kinetics

Xie et al, ACS Nano 8, 9606 (2014)
MXene and MoS$_2$ Heterostructure

Mg$^{2+}$ interacts strongly: High electrochemical V

Mg$^{2+}$ diffuses fast: fast kinetics
Voltage during uptake of Mg into MXene:MoS2

Stable voltage during discharge
Diffusion of Mg MXene:MoS$_2$

We expect fast kinetics on MoS$_2$ surface
By increasing the interlayer distance, diffusivity is enhanced, while retaining a high electro-chemical voltage!

Aseem Kshirsagar and U V Waghmare (2017)
Summary

First-principles calculations:

*Predict structure, properties and functionality of materials*

Potential for applications in Energy Conversion and Storage

Photocatalysts, Electro-catalysts, photo-voltaics, Catalyst for fuel cell, Cathodes for batteries

From Electronic Structure to Electrochemistry
Thank You!