ASESMA

African School for Electronic Structure Methods and Applications

The second decade and its role in new initiatives for scientific research

Richard M. Martin
University of Illinois and Stanford

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Why
Electronic Structure
Theory
(with no equations!)
Role in Research Today

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The second decade and its role in new initiatives for scientific research

Role of theory

1) Research in all fields today
2) Research at Light Sources

Richard M. Martin
University of Illinois and Stanford

ASESMA

A 10-year program from 2010 to 2020

Endorsed by IUPAP (International Union of Pure and Applied Physics)
Supported by ICTP (International Centre for Theoretical Physics) , …..

Schools each 2 years to foster
a collaborative network for research and higher education within Africa

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A new larger vision for ASESMA – 2020-2030

Endorsed by IUPAP for a second decade
Based on accomplishments in the first 10 years

More emphasis on
Problems related to biology
Machine Learning
……

The key is the long term support of ICTP and IUPAP

The ASESMA Approach

Computational Science

The core guiding principle is that computation makes it possible to do world-class research with modest investment. Computation is important in every area of science and technology.

Choice of Topics

Electronic structure is an important field that is narrow enough to build up a network for joint work and collaboration, yet broad enough to span the range from fundamental physics to applications in materials science, chemistry, and many other fields.

An ASESMA school

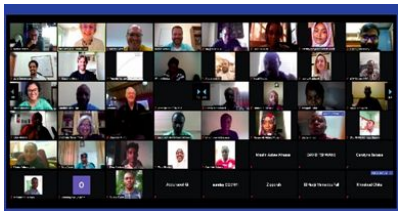
Typically ~ 1/2 participants new to the field, 1/2 returning to increase their knowledge, collaborate, and tutor the new people.

Each school includes basic theory and methods and hands-on computing.
Each participant is involved in a project in an area of current research.

ASESMA Schools

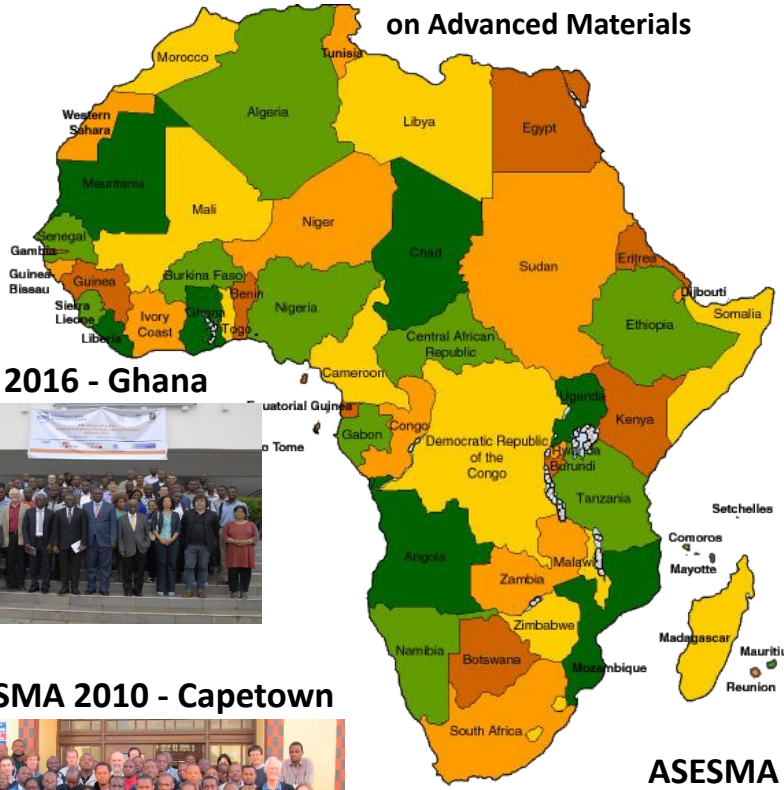
279 participants from 29 African countries (2008 -2023)

ASESMA 2021 - Virtual
(Showing only Lecturers, Mentors)



Now Many Active Research Groups!

Sudan 2013, 2015, 2017
Tutorials at Khartoum Workshop on Advanced Materials



ASESMA 2018 - Ethiopia

ASESMA 2012 - Kenya

Regional workshops
(Mini-ASESMAs)
Republic of Congo – 2017, 2021, 2023
Dem. Rep. of Congo - 2022
Cameroon 2018, 2019, 2022
Ethiopia – 2021
Kenya - 2021, 2022, 2023
Rwanda - 2019, 2023
South Africa – 2019, 2022
Tanzania - 2019

ASESMA 2016 - Ghana

ASESMA 2023-Rwanda

Sessions at African Materials Science Society
Botswana – 2017
Tanzania – 2019
Senegal - 2022

ASESMA 2010 - Capetown

ASESMA 2015 - Johannesburg

2008 - Capetown - Workshop that led to foundation of ASESMA

Active Research Groups

Indicating countries,
many (most!) with several active groups

These are teachers of future scientists/citizens!

Sponsors – so far

IUPAP
International Union of Pure and Applied Physics

Board on International Scientific Organizations
U.S. Liaison Committee for IUPAP
National Academy of Sciences

ICTP
The Abdus Salam International Centre for Theoretical Physics

UNESCO
United Nations Educational, Scientific and Cultural Organization

EAIFR
ICTP - East African Institute for Fundamental Research under the auspices of UNESCO

APS physics

NSF

THE THOMAS YOUNG CENTRE TyC

APS INNOVATION FUND
Accepting proposals for APS mission-focused projects
if

MARVEL
NATIONAL CENTRE OF COMPETENCE IN RESEARCH

NITheP
National Institute for Theoretical Physics

Why Electronic Structure?

Electronic Structure is one of the grand challenges of physics

With Application to Physics, Chemistry, Materials Science, and many other areas

Electronic Structure is one of the grand challenges of physics

Many-Body problem of interacting electrons and nuclei in molecules, solids, liquids, ….

Two Equations!

We must solve the many-body Schrodinger Equation

$$\hat{H}|\Psi\rangle = E|\Psi\rangle$$

Kinetic energy of electrons

electron-nuclei interactions

electron-electron interactions

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

The reason to show the equations is to emphasize that we are dealing with the REAL problem - not some model!

Electronic Structure is one of the grand challenges of physics

Many-Body problem of interacting electrons and nuclei in molecules, solids, liquids, ….

We can understand the challenges without Equations!

We must solve the quantum mechanics problem

of Many Interacting Electrons

The Hard Problem
The Grand Challenge

in a system defined by the Nuclei

Vast array of Problems
Must be solved accurately

Density Functional Theory (DFT)

Hohenberg-Kohn Theorem

All properties of the system are determined by the ground state density $n_0(r)$

Function of r
3 dimensions

Sounds like magic! How can this possibly be true?

Answer

1. All properties of the system are determined by the potential acting on the electrons (due to the nuclei) $V_{ext}(r)$

Function of r
3 dimensions

2. HK showed there is a one-to-one correspondence $V_{ext}(r) \rightleftharpoons n_0(r)$

3. Therefore all properties of the system are determined by $n_0(r)$

   Each property is a functional of $n_0(r)$: $F[n_0(r)]$

But

The "theorem" gives no way to calculate any property except to solve the original problem!

A Nobel Prize for that?

The Kohn-Sham Auxiliary System

This is the idea worth a Nobel Prize!

Construct a soluble independent-particle problem with density equal to the density $n_0(r)$ of the full interacting electron problem

$$\text{Energy} = E_{\text{Ind. part.}} + E_{xc}[n_0]$$

Soluble on a computer!
Many very efficient codes

All the hard parts of the problem!
(Exchange-correlation)

A Nobel Prize because this construction made possible accurate approximations for $E_{xc}[n_0]$

How useful is it?

There are good approximations!

LDA - Local density approximation, proposed by Kohn and Sham in the 1964 paper

GGAs - Generalized Gradient approximations

Hybrid – GGA + Hartree-Fock

. . . . .

Now an essential part of research!

Calculations of structures – lattice constants with ~1% accuracy

-- phonons ~5% accuracy

-- structures of molecules ……

Useful approximations for many other properties

Physics, Chemistry, Materials science, Engineering, . . .

How useful is it?

The Kohn-Sham papers are the most widely cited papers in Physics

The ability to do accurate calculations of the minimum energy structure of a complex solids and molecules has transformed research!

Approximately 50,000 papers per year!

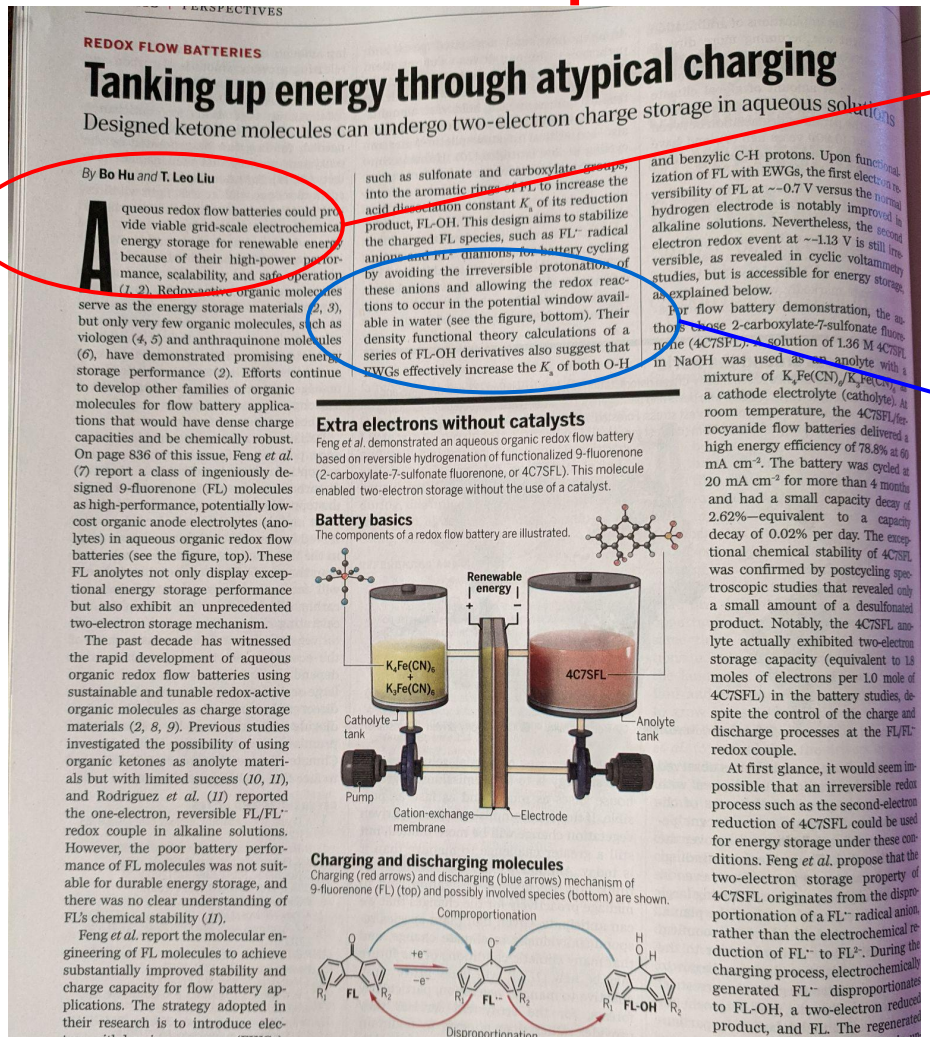
(Estimate based on current trends and a study of the literature 10 years ago, which found ~30,000 papers per year.)

I made a little survey of papers in Nature and Science

Of all papers on experimental materials at the atomic level almost 1/2 involved DFT calculations working together with experiments

Electronic Structure Calculations are REALLY USEFUL !

Example in Science Magazine



PERSPECTIVES

REDOX FLOW BATTERIES

Tanking up energy through atypical charging

Designed ketone molecules can undergo two-electron charge storage in aqueous solutions

By **Bo Hu** and **T. Leo Liu**

Aqueous redox flow batteries could provide viable grid-scale electrochemical energy storage for renewable energy because of their high-power performance, scalability, and safe operation (*1*, *2*). Redox-active organic molecules serve as the energy storage materials (*2*, *3*), but only very few organic molecules, such as viologen (*4*, *5*) and anthraquinone molecules (*6*), have demonstrated promising energy storage performance (*2*). Efforts continue to develop other families of organic molecules for flow battery applications that would have dense charge capacities and be chemically robust. On page 836 of this issue, Feng *et al.* (*7*) report a class of ingeniously designed 9-fluorenone (FL) molecules as high-performance, potentially low-cost organic anode electrolytes (anolytes) in aqueous organic redox flow batteries (see the figure, top). These FL anolytes not only display exceptional energy storage performance but also exhibit an unprecedented two-electron storage mechanism.

The past decade has witnessed the rapid development of aqueous organic redox flow batteries using sustainable and tunable redox-active organic molecules as charge storage materials (*2*, *8*, *9*). Previous studies investigated the possibility of using organic ketones as anolyte materials but with limited success (*10*, *11*), and Rodriguez *et al.* (*11*) reported the one-electron, reversible FL/FL$^{\cdot-}$ redox couple in alkaline solutions. However, the poor battery performance of FL molecules was not suitable for durable energy storage, and there was no clear understanding of FL's chemical stability (*11*).

Feng *et al.* report the molecular engineering of FL molecules to achieve substantially improved stability and charge capacity for flow battery applications. The strategy adopted in their research is to introduce electron-withdrawing groups, such as sulfonate and carboxylate groups, into the aromatic rings of FL to increase the acid dissociation constant K_a of its reduction product, FL-OH. This design aims to stabilize the charged FL species, such as FL$^{\cdot-}$ radical anions and FL^{2-} dianions, for battery cycling by avoiding the irreversible protonation of these anions and allowing the redox reactions to occur in the potential window available in water (see the figure, bottom). Their density functional theory calculations of a series of FL-OH derivatives also suggest that EWGs effectively increase the K_a of both O-H and benzylic C-H protons. Upon functionalization of FL with EWGs, the first electron reversibility of FL at ~−0.7 V versus the normal hydrogen electrode is notably improved in alkaline solutions. Nevertheless, the second electron redox event at ~−1.13 V is still irreversible, as revealed in cyclic voltammetry studies, but is accessible for energy storage, as explained below.

For flow battery demonstration, the authors chose 2-carboxylate-7-sulfonate fluorenone (4C7SFL). A solution of 1.36 M 4C7SFL in NaOH was used as an anolyte with a mixture of $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ as a cathode electrolyte (catholyte). At room temperature, the 4C7SFL/ferrocyanide flow batteries delivered a high energy efficiency of 78.8% at 60 mA cm^{-2}. The battery was cycled at 20 mA cm^{-2} for more than 4 months and had a small capacity decay of 2.62%—equivalent to a capacity decay of 0.02% per day. The exceptional chemical stability of 4C7SFL was confirmed by postcycling spectroscopic studies that revealed only a small amount of a desulfonated product. Notably, the 4C7SFL anolyte actually exhibited two-electron storage capacity (equivalent to 1.8 moles of electrons per 1.0 mole of 4C7SFL) in the battery studies, despite the control of the charge and discharge processes at the FL/FL$^{\cdot-}$ redox couple.

At first glance, it would seem impossible that an irreversible redox process such as the second-electron reduction of 4C7SFL could be used for energy storage under these conditions. Feng *et al.* propose that the two-electron storage property of 4C7SFL originates from the disproportionation of a FL$^{\cdot-}$ radical anion, rather than the electrochemical reduction of FL$^{\cdot-}$ to FL^{2-}. During the charging process, electrochemically generated FL$^{\cdot-}$ disproportionates to FL-OH, a two-electron reduced product, and FL. The regenerated

Extra electrons without catalysts

Feng *et al.* demonstrated an aqueous organic redox flow battery based on reversible hydrogenation of functionalized 9-fluorenone (2-carboxylate-7-sulfonate fluorenone, or 4C7SFL). This molecule enabled two-electron storage without the use of a catalyst.

Battery basics

The components of a redox flow battery are illustrated.

Charging and discharging molecules

Charging (red arrows) and discharging (blue arrows) mechanism of 9-fluorenone (FL) (top) and possibly involved species (bottom) are shown.

Aqueous redox flow batteries could provide viable grid-scale elecrochemical energy storage for renewable energy because ……

density functional theory calculations of a series of FL-OH derivatives also suggest that ……

One must go beyond DFT for many things!

Kohn-Sham DFT is amazing good for structures:
Where are the atoms?
What are vibration frequencies?

But DFT is NOT meant to give spectra correctly

Often very bad - "The band gap problem"

For Spectra one needs methods like:
Time-dependent DFT
Many-body perturbation theory (The GW method, etc.)

It is a hard problem!

There is great experience in how to understand and use the methods!

ASESMA

Core Topics + Hands-on Tutorials and Projects

Density Functional Theory

Alberto Carta - Mentor helping students in DFT project in 2023

Quantum Chemistry and molecular systems

Marc Casida – pioneer of time-dependent DFT with project in 2023

Many-body methods for spectroscopy

Azima Seidu from Ghana in 2016 with the lecturers Andrea Marini and Matteo Gatti (Afterward Azima visited Gatti in France.)

Three ASESMA participants are working in Gatti's group right now!

Machine Learning

Alex Urban leading project in 2023

ASESMA

Results (in addition to the ASESMA network!)

Just a few Examples

ASESMANet
Program for providing small amounts of funds for meetings and collaborations

US-Africa Initiative of the American Physical Society
Next slide

One example of a collaborations started in ASESMA

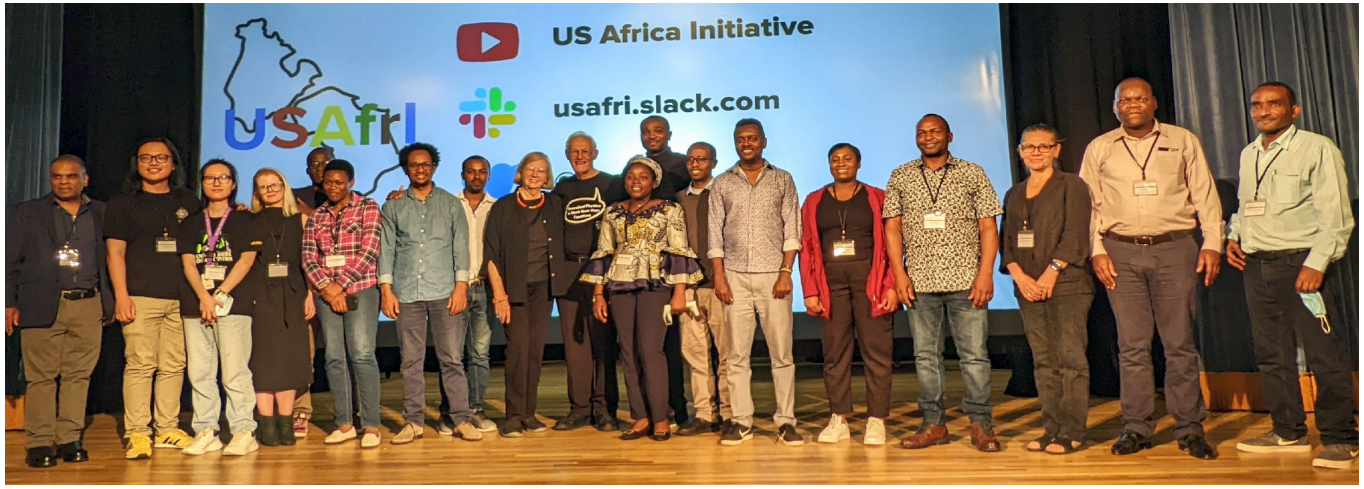
US Africa Initiative for Electronic Structure (USAfrI)

Sponsored by the APS
2019 Innovation Fund

USAfrI was created by a grant from the APS with the far-reaching goal

"to create a platform for exchange between African and U.S. physicists with opportunities to have a major impact on research and education in Africa."

The APS funded a set of workshops and visits of
15 African Scientists to Universities and Labs in the US to initiate collaborations



It could happen only because of ASESMA and the network of African scientists at a level to fully participate in global community

USAfrI finished in 2022. What is needed is long-term support!

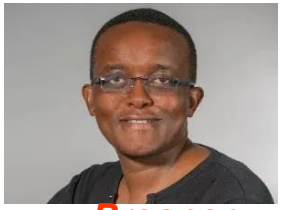
USAfrI is just an example of what can be done._There is great interest and willingness to participate. Over 100 US scientists were definitely interested in USAfrI!

For more information see
https://usafricainitiative.org/

Results of ASESMA: One Example

2010 Prosper Ngabonziza attended ASESMA when he was a student

2012 Several times Prosper proposed making experiment/theory project in ASESMA



Prosper

2015 Garu Gebreyesus attended ASESMA

Had not worked in Electronic Structure before

Organized ASESMA in 2016 in Ghana!

Garu in audience in 2015

2020 Started ASESMA collaboration (Ghana, Nigeria, Rwanda, Italy, Germany, US) based on Prosper's experimental work

Photoemission (ARPES) on $Sr_4Ru_3O_{10}$

Phys. Rev. paper in 2022

2022 New Idea from that work led to new collaboration with experimentalists at Advanced Light Source In US

Remote Access!

Paper submitted 2023

Jonathan Denlinger

2023 New Discoveries from that work are leading to further work

Results of ASESMA: One Example

A successful collaboration!

Young physicists Prosper and Garu experiment/theory collaboration with help from senior people in theory and experiment

2 papers and new discoveries (confirmation of theory and additional unexpected discoveries!) leading to further work

What could be better?

For this to be standard - not take 13 years!
Scientists working together with local support (funding, colleagues) as part of the global community

Role of ASESMA for the future

Theoretical calculations are an essential part of research!

Can be world class with much less cost than experimental facilities!

Any Major Research Project needs a theory component

Especially a light source!

Theory should not be "and add-on"

It should be part of planning from the start

Example:

There is now remote access for experiments at light sources in the US and elsewhere. The LAAAMP program provides the possibility for a professor and a student to visit a Lab to learn techniques and use remotely or in person

A multiplier effect!

Combining with theory at the start can build up expertise for analysis, choosing experiments, teaching students, …..

Low cost and -- more important -- an essential part of science