LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications

SD1: Electronic and Magnetic Materials

FOCUS 1

Computational Methods for Strongly Correlated Materials

FOCUS 2

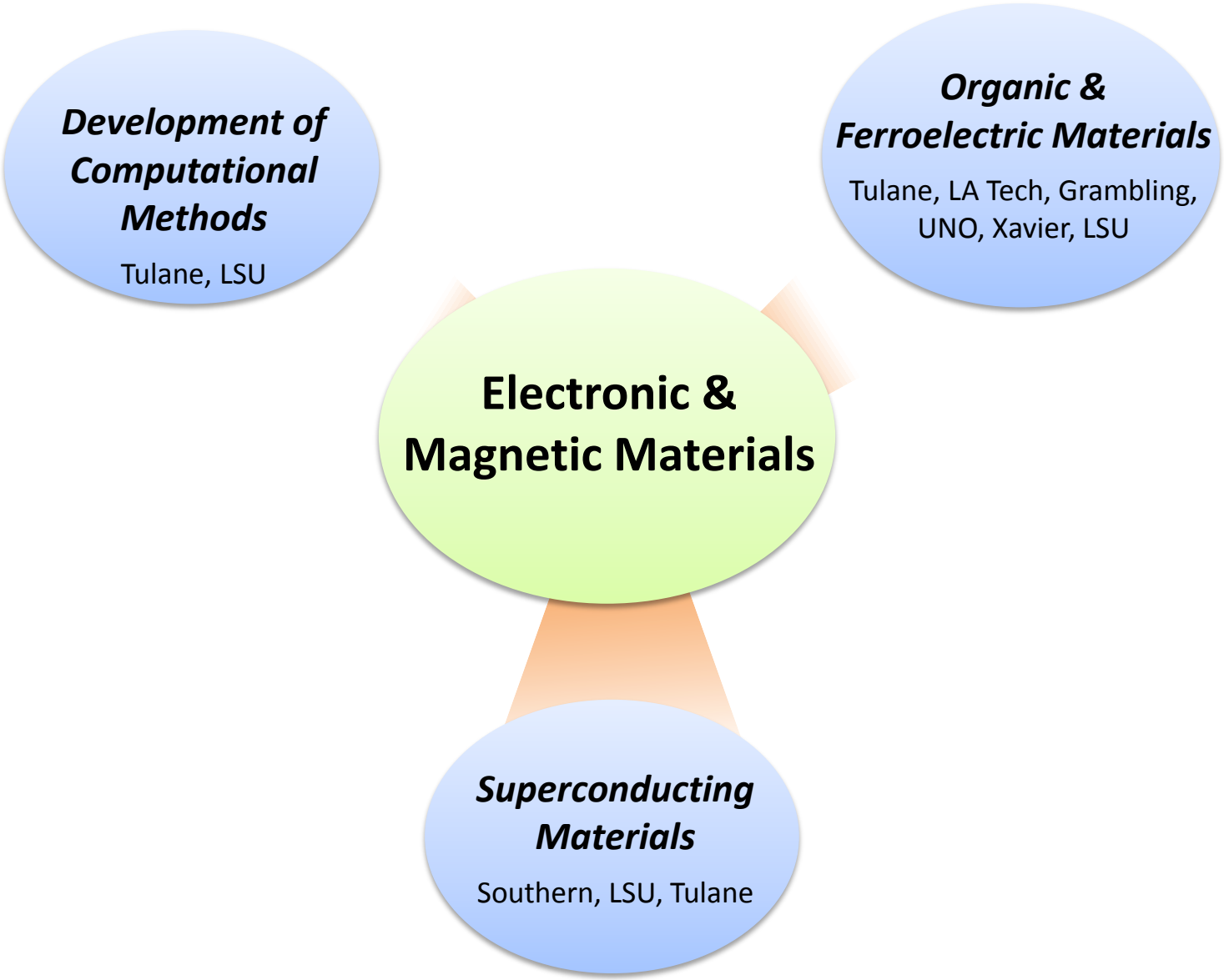
Correlated Organic & Ferroelectric Materials

FOCUS 3

Superconducting Materials

Xavier University of Louisiana · Southern University · LSU Louisiana State University · Louisiana Tech · Grambling State University · UNO University of New Orleans · Tulane University

SD1 Research Themes



OUTLINE

Introduction to Science Driver 1

SD1 Research Accomplishments and Milestone Scorecards for the Past Year of LA-SiGMA Support, in Each of the Three Focus Areas

(No milestone for Columbus or Einstein!)

THE GOAL OF SCIENCE DRIVER 1 IS TO DEVELOP AND TEST NEW COMPUTATIONAL FORMALISMS, ALGORITHMS, AND CODES WHICH WILL EVENTUALLY ENABLE THE SEARCH FOR NEW CORRELATED MATERIALS ON THE SUPERCOMPUTER.

Thus SD1 must confront the electron-electron interaction. Correlated many-body methods, including *Quantum Monte Carlo* (QMC), are computationally inefficient for systems of many electrons. One way to deal with this problem is to perform multiscale calculations, where QMC is used to treat electron-electron correlations only on the shortest length scales.

More-approximate methods are then applied on longer length scales.

The other and more common way is to use the Kohn-Sham *density functional theory* (DFT), an orbital-based approach in which the electron exchange-correlation energy as a functional of the electron density is approximated. The remaining problems are: a) to improve the accuracy of the available approximations; b) to understand long-range correlations including van der Waals interactions; and c) to deal with the fact that even the exact Kohn-Sham band structure can underestimate the *fundamental energy gap of a solid*.

SD1 also includes *experimental and computational studies of strongly-correlated materials*.

SD1 FOCUS 1: PREDICTIVE METHODS FOR CORRELATED MATERIALS

MULTISCALE METHODS FOR DISORDERED & INTERACTING SYSTEMS

Mark Jarrell, Juana Moreno, C.E. Ekuma, S. Feng, Z. Meng, C. Moore, and R. Nelson (LSU)

Solutions for model Hamiltonians

(Ising-model glasses and Quantum Monte Carlo or QMC) found to be greatly accelerated by graphics processing units (GPU's). With the CTCI team, developing QMC codes for the next generation of GPU supercomputers.

Incorporation of nonlocal correlations:
Proposed a new Cluster Typical Medium Theory, which permits the study of Anderson localization in both model- and real disordered materials, unlike the Coherent Phase Approximation and its cluster extensions.

Treatment of three length scales for the size extrapolation of correlation in large systems
Shortest: explicit or exact correlation
Intermediate: perturbation theory
Longest: mean-field correlation

Applied to the two-dimensional Hubbard model.

Construction of effective interacting Hamiltonians

Generate a band structure for (Ga,Mn) As and (Ga,Mn)N, from Kohn-Sham density-functional theory.

Apply a Wannier-function-based downfolding.

ACCURATE BAND GAPS FROM DENSITY FUNCTIONAL THEORY

Diola Bagayoko and collaborators

To be presented at the end of the SD1 talk.

SD1, F1-3

DENSITY FUNCTIONAL THEORY: VAN DER WAALS INTERACTION AND META-GGA

John P. Perdew, Jianmin Tao, and Adrienn Ruzsinszky (Tulane)

van der Waals (vdW) expansion for the vdW interaction between two spherical electron densities at large separation d between the centers:

$$-C_6/d^6 \; -C_8/d^8 \; -C_{10}/d^{10} - \ldots$$

The coefficients are typically known only in low orders of d^{-1} and only between small objects. vdW is an important interaction between closed-shell systems in physics, chemistry, & biology.

SD1, F1-4

Spherical-shell model

A conducting uniform valence electron density between an outer and an inner radius. Exact analytical expressions for the dynamic multipole polarizabilities and thus the exact vdW coefficients to second order in the electron-electron repulsion and to all orders in d^{-1} . The model is usefully accurate for quasi-spherical nano-structures (solid spherical clusters and fullerene shells like C_{60}).

Surprising size-dependence of vdW coefficients between identical nanostructures

Each object has *n* atoms. Then $C_6 \sim n^2$ for solid clusters, as predicted by the atom pair-potential picture. But $C_6 \sim n^{2.75}$ for fullerenes. Surprisingly, large fullerenes cannot be described correctly either by the atom pair-potential picture or by standard nonlocal correlation energy functionals, which both underestimate their vdW interactions.

SD1, F1-5

vdW interaction as a summable asymptotic series

A study of the high-order vdW coefficients shows that the vdW expansion can be summed to all orders. The sum diverges when the spheres touch ($d=R$). This unphysical divergence is removable by making exponentially-decaying additive corrections to d, since the expansion is only asymptotic (for large d).

Meta-generalized gradient approximation

The revTPSS 2009 meta-GGA is a computationally-efficient nonempirical density functional for the exchange-correlation energy in the absence of nonlocal effects like long-range vdW. It is accurate for many properties of atoms, molecules, and solids. But it still has formal problems and unexpected errors, as for the structural phase transitions of solids. A better meta-GGA will be developed in the next year.

SD1 Focus 1 Milestones and Score Card

Milestones	Y 1	Y 2	Y 3	Y 4	Y 5	
Develop QMC solver for GPU accelerated supercomputers.	X	X				*On Track*
Incorporate Hyper-GGA functionals into common DFT codes including VASP.	X	X	X			*REV-TPSS incorporated; ongoing*
Develop MSMB solver able to treat multiple correlated orbitals.	X	X	X	X		*On Track*
Port hyperparallel codes to NSF national leadership class machines (Blue Waters).	X	X	X	X	X	*Ahead of Schedule*

SD1; F1

SD1 FOCUS 2: CORRELATED ORGANIC AND FERROELECTRIC MATERIALS

CONDUCTING METALLOPOLYMERS

J. Garno (LSU); P. Derosa, N. Ranjitkar, B. Ramachandran,
S. Poudel (LaTech); M. Jarrell, J. Moreno, and A. Paudyal (LSU)

Organic conductors are of interest for flexible electronic and solar cells. Polythiophenes are polymerized thiophenes or sulfur hetero-Cycles that can become conducting with doping of their conjugated pi orbitals. Experimental and computational studies have been carried out for polythiophenes containing in-chain cobalt and manganese carborane centers with delocalized electrons.

J. Garno performed atomic force microscopy surface studies and conducting probe measurements for these novel cobalt carboranes.

P. Derosa and N. Ranjitkar used the code Gaussian09 to simulate the structures and spin, finding that the ground state is a spin singlet for the cobalt carborane but not for the manganese, according to a variety of density functionals.

They also computed the conductivity of the cobalt carborane, in agreement with Garno's measurement, using Green's functions on top of the density functional calculation.

SD1, F2-2

MAGNETIC AND MULTIFERROIC MATERIALS

S. Whittenburg , G. Caruntu, L. Malkinski (UNO)
A. Burin (Tulane)
P. Kucheryavy, G. Goloverda, and V. Kolesnichenko (Xavier)
R. Kurtz, P. Sprunger, and John DiTusa (LSU)

Multiferroic materials exhibit both ferromagnetic and ferro-electric behavior, and thus have potential device applications.

S. Whittenburg expanded his micromagnetics code to include ferroelectric materials, and correctly predicted the ferroelectric phase transition of $BaTiO_3$.

SD1, F2-3

G. Caruntu developed a novel experimental technique for the local measurement of strain-mediated magneto-elastic coupling in nanocomposite films.

L. Malkinski has developed new techniques to form multiwall microtubes of magnetic or piezoelectric materials. He also explored liquid crystal/ferromagnetic nanoparticles.

A. Burin used density functional software (Gaussian09, ORCA) to model nanoscopic iron oxide clusters, finding a high-spin (S=12) ground state. P. Kucheryavy, G. Goloverda, and V. Kolesnichenko developed a method of synthesis for ultramall (2.7-11 nm sizes) and with strong potential for use as contrast-enhancing MRI agents..

R. Kurtz and P. Sprunger investigated the magnetic properties of FeAl, which semilocal density functionals predict to be ferromagnetic, in disagreement with experiment and with DFT+U calculations. Measurements at CAMD found no surface magnetism. SD1, F2-4

SD1 Focus 2 Milestones and Score Card

Milestones	Y1	Y2	Y3	Y4	Y5	
Test array of DFT functionals for prediction of metalloporphyrin and ferroelectric properties.	X	X				*On track with different systems*
Prepare and measure electrical/magnetic properties of metalloporphyrin nanostructures.	X	X				*On track with different systems*
Prepare organic magnets and ferroelectrics.	X	X	X			*On track*
Develop experimentally validated computational models for porphyrin systems using magnetoresistance and electrical conductance measurements as guides	X	X	X	X	X	*On track*
Develop multiscale models of metalloporphyrin systems using DFT parameters			X	X	X	
Predict charge transport in metalloporphyrins and compare with experiments			X	X	X	
Predict properties of ferroelectrics using new nonlocal meta-GGA DFT functionals			X	X	X	
Develop experimentally validated models of organic magnets and ferroelectrics			X	X	X	

SD1; F2

J. DiTusa investigated magnetism and electrical transport of transition metal silicides, germanides, and gallium compounds.

IRON-BASED SUPERCONDUCTORS AND RELATED MATERIALS

L. Spinu (UNO)
Z. Mao (Tulane)
W. Plummer, V.B. Nascimento, and D.D. dos Reis (UNO)

Since their discovery in 2008, iron-based superconductors have generated intense scientific interest, since their complex interplay between magnetism and superconductivity suggests that the attraction pairing the electrons is provided by spin fluctuations.

The penetration depth of a magnetic field can give information about the pairing mechanism. L. Spinu has measured the penetration depth in single crystals at ultra-low temperature.

Z. Mao has synthesized a new layered iron pnictide CuFeSb, that exhibits an unusual metallic ferromagnetic state instead of the usual antiferromagnetic or superconducting states, suggesting a competition between antiferromagnetism and ferromagnetism.

The competition between phases in strongly-correlated materials occurs in the surface as well as in the bulk. W. Plummer's group is measuring surface structure in complex materials via LEED. They have developed codes to invert the LEED data to find the surface structure.

SD1 Focus 3 Milestones and Score Card

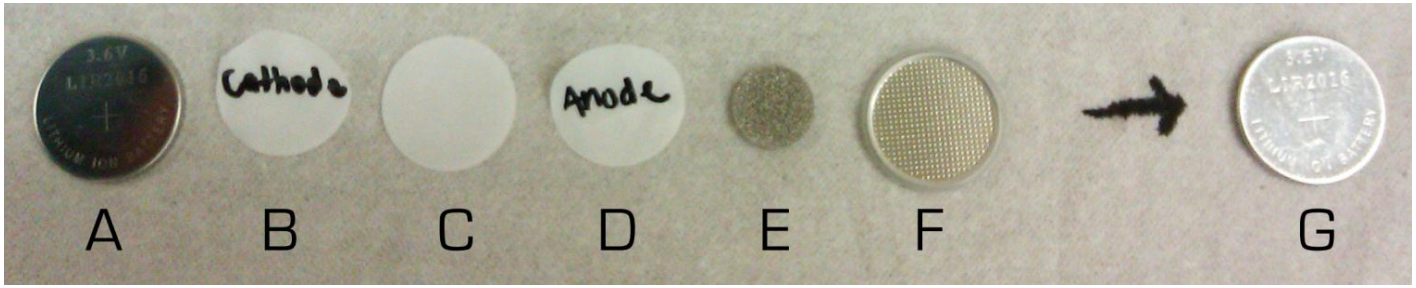
Milestones	Y1	Y2	Y3	Y4	Y5	
Address the bottlenecks and numerical instabilities in the parquet equations by employing better parallel linear systems solvers and develop multiband parquet codes.	X	X	X	X	X	*On Track*
Incorporate latency hiding methods into parquet codes.	X	X				*On Track*
Use hybrid QMC to address the origin of the QCP and competing order in cuprate models.	X	X	X			*On Track*
Study overscreening in pnictide models using new Hyper-GGA functionals .	X	X	X			*In Progress with modifications*
Use methods that combine LDA models obtained from downfolding and DCA/MSMB to study correlation and phonon effects in the pnictides.	X	X	X	X	X	*On Track*

SD1; F3

Outreach Activities (Tulane)

- Provided summer research opportunities for the undergraduates supported by the LA-SiGMA REU program. Two students from this program worked with Prof. Mao last summer and they were involved in the research searching for novel superconductor in iron chalcogenides using chemical intercalation.
- Outreach activity

Offered research opportunities to students from Benjamin Franklin High School (BFHS) in New Orleans. Prof. Mao has directed two students from BFHS to complete their independent research project. This project aimed at searching for alternative cathode materials for developing high energy density lithium-ion battery. This project was successful; some promising materials have been found.



Assembly of a lithium ion coin cell. (A) positive terminal; (B) cathode; (C) insulator; (D) anode (lithium); (E) current collector (nickel foam); (F) negative terminal; (G) completed lithium ion coin cell

Preparation of cathode

Outreach

- Nanodays. LA-SiGMA faculty members gave four public lectures and graduate students led demonstrations at the BREC's Highland Road Observatory and the Louisiana Arts and Science Museum: over 300 visitors.
- CCT and LA-SiGMA REU programs

Outreach, education, funding initiatives (Garno)

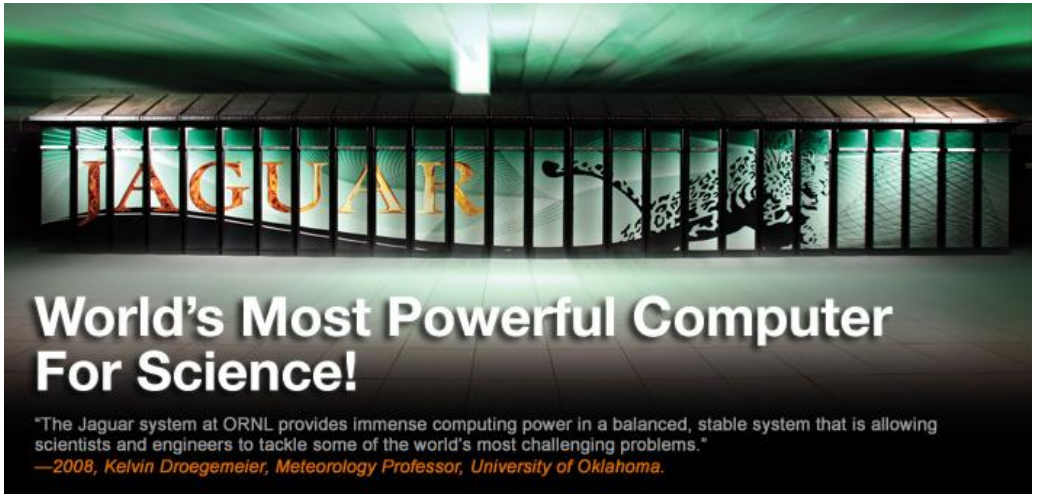
- *NanoDays*
- *Super Science Saturday*
- *Chem Demos,*
- *Saturday Science*

Graduate Student Education

- Distance Learning Courses:
  - Computational Solid State Physics
  - Advanced Solid State Physics with Computation
  - Computational Physics
  - Simulations of Quantum Many-Body Systems
  - …Ten courses total
- SD1 International Computational Materials Science Seminar Series (EVO)
  - Wednesdays at 10:00
  - (http://www.institute.loni.org/lasigma/lasigma-int-seminarseries.php)
  - Kieron Burke, Karol Kowalski, Bayo Lau…
- GPU Team Meetings
  - Monday, 12:30-1:30 (EVO)
  - Team meetings for various GPU projects

Partnership with Pacific Northwest National Lab

- Environmental Molecular Sciences Laboratory (EMSL)
  - Home of NWChem!
- Invited DOE Center request ($11M)
- Internship program for LA-SiGMA students
  - 3-6 month visits
  - Working with EMSL Open Source Code Developers
  - undergraduate to PhD
- NWChem workshop



EMSL Associate Lab Director Bill Shelton participating in LA-SiGMA REU panel

Pacific Northwest
NATIONAL LABORATORY

Funding

- Two Computational Materials Science and Chemistry Network awards (BNL, Ames, SLAC, Argonne, PNNL)
- NSF CRI Award
  - About $500K
  - Shelob Cluster available to LA-SiGMA investigators
- SciDAC request (submitted)
- DOE Center request (invited)
- NSF SAVI request (white paper).
  - Extend LA-SiGMA into an international virtual org.

A Solution to the Band Gap Problem

The following slides report on a solution to the band gap underestimation by theoretical calculations.

Contributors to the numerical results reported include: *Bagayoko, G. Zhao, L. Franklin, and Y. Malozovsky*, at **SUBR**, and *C. E. Ekuma, M. Jarrell, and J. Moreno*, at **LSU**.

Future contributors to this line of research include *Dr. A. Stewart, Dr. S. Yang, and Mr. Bethuel Khamala* at **SUBR**

Yes, we are looking for contributors on other LASiGMA campuses to which we can provide our computational package whose design, unlike that of most pseudo potential codes, permits the implementation of the BZW-EF Method

THE BAND GAP UNDERESTIMATION BY THEORY

Illustrative Discrepancies between the Measured and Calculated Band Gaps of **ZnO** in the Wurtzite Structure

EXP1	EXP2	LDA 1	LDA2	LDA3	GGA1	GW1	GW2	HF
3.44 eV	**3.30 eV**	0.78 eV	1.15 eV	2.26 eV	0.77 eV	2.44 eV	4.28 eV	8.61 eV*
Low T	Room T	0 T	0 T	0 T	0 T	0 T	0 T	0 T

Exp: Experiment, **LDA**: Local Density Approximation, **GW**: Green Function and Screened Coulomb Approximation; **HF**: Hartree Fock Method

Similar discrepancies are found for elemental, binary, tertiary, and quaternary semiconductors and insulators. These failures of theory have prevented it from informing and guiding the design and fabrication of device and of novel materials.

The Inherently Coupled Equations of the Local Density Approximation (LDA) of DFT- Once V_{xc} is Selected

Source: . W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

EQUATION 1 (Only for the ground state)

$$\left[-\frac{1}{2}\nabla^2 + V(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d\vec{r}' + V_{xc}(n(\vec{r}))\right]\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

Equation 2 (Sum over occupied states only)

$$n(\vec{r}) = \sum^{N} \psi^*(\vec{r})\psi(\vec{r})$$

Sum over **occupied** states only

OUR COMPUTATIONAL APPROACH

A. THE LCAO (LCGO) FORMALISM

THE EIGENVALUE EQUATION, $H\psi = E\psi$, IS SOLVED SELF- CONSISTENTLY BY USING the linear combination of atomic (or Gaussian) orbitals – LCAO (LCGO):

$$\Psi = \sum_{i=1}^{N} a_i \Phi_i, \text{ i = 1, N}$$

B. THE POTENTIAL

We utilize **the LDA potential** by Ceperley and Alder - as parameterized by Vosko, Wilk, and Nusair (VWN) and

The generalized gradient approximation (GGA) potential of Perdew and co-workers (including Burke, Ernzerhof, Wang, and Zunger).

C. The Bagayoko, Zhao, and William (BZW-EF) Method

This method appears to have resolved the close to 70 years old energy and band gap problem to have **ushered in an era predictive calculations that are transformative and have many practical applications in industry.**

A SOLUTION TO THE "GAP" PROBLEM

It simply consists of solving the system of equations as opposed to just the Kohn-Sham equation. (Circumstances have it that one can unwittingly take the latter for the former).

To solve the system of equations, one starts with small basis set (one no smaller than the minimum basis set) to perform a self-consistent calculation. Other calculations follow, as explained in AIP Advances 2, 012189 (2012), **until the occupied energies reach their minima**.

The knowledge of the Rayleigh theorem allows one to identify the optimal basis set: **the smallest basis set that leads to the minima of all the occupied energies**. Basis sets larger that the optimal one (and that contain it) do not change the occupied energies, even though they lower several unoccupied ones! This extra-lowering is an artifact of the Rayleigh theorem.

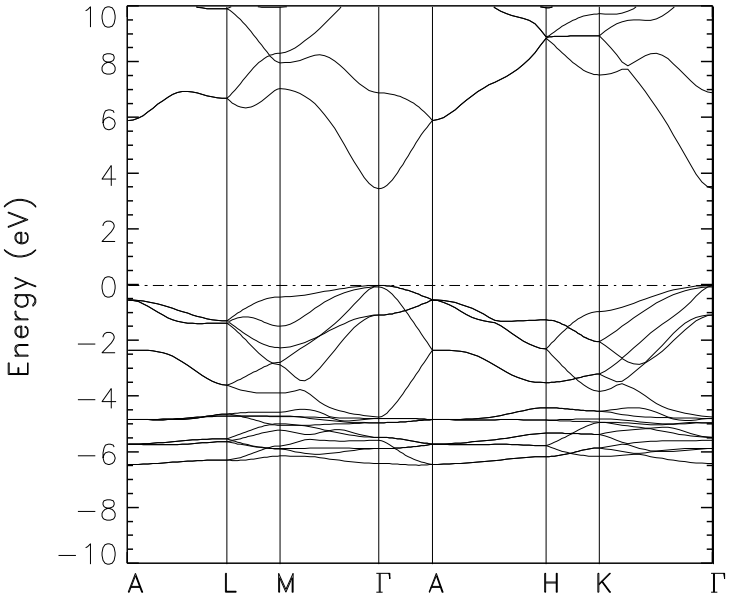
ILLUSTRATIVE RESULTS

Calculated Properties (Band Gaps) of Selected Semiconductors versus Measured Values. [Computations done in accordance with the BZW-EF method for **TiO_2 ,** ZnO, Ge, and **$SrTiO_3$**, and BZW for the others]

w-InN	Prediction	Measurement	c-InN	Predictions	Measurement
Eg	0.88 eV	0.7-1.0 eV	Eg	0.65 eV	0.61 eV
c-$SrTiO_3$	**Calculation**	**Measurement**	Lat. Cst	A = 5.017 Å	A =5.01±0.01 Å
Eg,ind	3.21-3.24 eV	3.10 – 3.25 eV	**c-Si_3N_4**	**Prediction**	**Measurement**
			Eg	3.68 eV	3.66 – 3.7 eV

TiO_2	**Calculation**	**Measurement**	**Ge**	**Calculation**	**Measurement**
Eg, dir.	3.05 eV	3.0 – 3.1 eV	Eg,ind	0.65 eV	0.66 eV
Eg, ind	**2.95 eV**	**Yet unknown**	**w-ZnO**	**Calculation**	**Experiment**
InP, Eg	1.40 eV	1.40 & 1.42 eV	Eg	3.4 eV	3.4 -3.5 eV

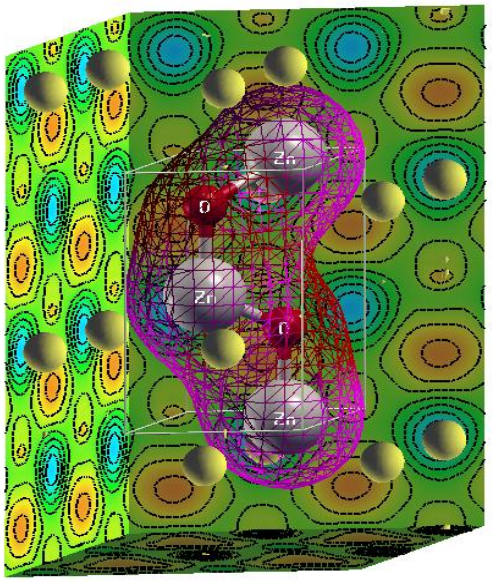
ILLUSTRATIVE RESULTS (Continued)



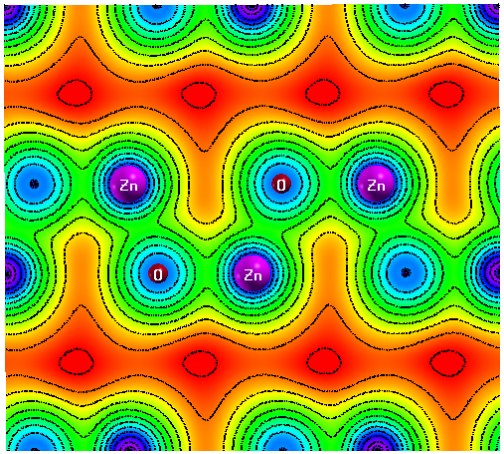
LDA BZW-EF band structures of ZnO
Eg = 3.4 eV, as found by experiment.

Manuscript to be submitted to the Canadian Journal of Physics.

The 2 graphs on the right explain the enhancement of BZW into BZW-EF: stopping the imposition of spherical symmetry on valence electrons that do not have it.



The unit cell of w-ZnO, with 2 O and the equivalent of 2 zinc sites inside it, along with the calculated crystalline isosurface and the molecular isosurface (in purple)
The work of Ekuma & Franklin show the primacy of p, d, & f symmetries over s (spherical) for valence electrons!



A 2-D contour plot of the electron charge density in w-ZnO. Note well that in the vicinity of atomic sites, one finds spherical symmetry. For the valence electrons, polarization (i.e., p. d. and f) prime spherical symmetry as found in the work of Ekuma and Franklin (EF)

IMPLICATIONS OF THE PREDICTIVE CAPABILITY OF THE BZW-EF

Molecular engineering, including the **prediction or design of novel molecules**, small or large, inorganic or organic- with known properties.

Semiconductor engineering, including the prediction or design of materials with desired band gaps – **particularly for tertiary and quaternary systems - and the study of defects, impurities, nanostructures, etc**.

Enhancement of simulations, partly by using accurate inter-atomic potentials or empirical pseudopotentials derived from BZW-EF results.

Theoretical exploration, using the nuclear shell model, of possibilities for **gamma ray amplification by stimulated emission of radiation (graser).**

Fundamental progress in the understanding of materials: i.e., a determination of the true capabilities and limitations of DFT, LDA, GGA, and of schemes (mostly non ab-initio) purporting to correct DFT (LDA, GGA, etc.) or to go beyond DFT altogether.

THANK YOU VERY MUCH FOR YOUR ATTENTION