*A Thermodynamic Density-Functional Theory and High-Performance Code
for Complex Materials with up to Multi-Million-Atom Unit Cells*

Report Date: 25 May 2012

Accomplishments FY11-present

As developed by Johnson and co-workers, **MECCA** (**M**ultiple-scattering **E**lectronic-structure **C**alculation for **C**omplex **A**pplications) is a Green's function KKR screened k-space code that scales as $O(N)$ for large-system sizes, even for metals (unlike for real-space KKR and LMTO methods). MECCA already addresses chemical disorder using the Coherent-Potential Approximation, a fully self-consistent and variational KKR-CPA.

Proposed work involved developments to make MECCA (an all-electron density-functional theory) code address accurately systems composed of 10^0 up to 10^6 atoms, which required fundamental and novel algorithms.

We have successfully developed, tested, and published methods that will permit the simulation of large-scale, accurate simulations using an all-electron DFT method.

Most importantly, as a major success, we have developed novel, fast algorithm for accurate solution to Poisson's equation for site-centered DFT techniques that avoids ill-convergent multipole methods and Fast-Fourier Transforms (FFT), which become ineffective due to communication problems on parallel architectures. Forces can now be determined in $O(N)$ cpu time in 10^3 to 10^6 atom simulations!

1. Algorithms Development for Application Code

For MECCA to address 10^4 to 10^6 atoms, several algorithmic developments were proposed, completed, and implemented for improved performance. As part of ongoing efforts, additional algorithms were developed outside of original proposal but necessary to accomplish goals of project.

Issues addressed include: reduced storage (e.g., for millions of potentials), improved representation to reduce basis set size (for computational efficacy), preconditioning, improved parallelization, generic potential generation, checkpointing, solution of Poisson's equations, forces, and Virial, etc.

Computer-Science Improvements

- **Reduced Storage:** Potentials and charge density storage via cubic-spline fits has been changed for reduced storage as necessary for large-scale applications: for 1,000,000 atoms, we reduced disk storage from 62 GB down to 8 GB without loss of accuracy ($\sim 8\times$ lower storage generally).
 - ✓ *Completed.* Further improvements are being studied to improve the digit accuracy of the splines for re-start of SCF iteration.
 - ✓ *Only recent machines could permit us to test MECCA.* Planned for 2012.

- *New Preconditioner for Iterative Inverses*: SPAI-C (pronounced “spicey”): A generalization of the SPAI (SParse-matrix Adaptive Inverse) algorithm was derived, implemented, and tested to address complex, non-Hermitian matrices inherent in multiple-scattering theory and MECCA. Testing for combined improvements of SPAI preconditioner and TF-QMR (transpose-free quasi-minimal residual) was completed.
 - ✓ For publication, an additional assessment of method in standard linear-algebra suite was request. Illinois graduate student plans to complete this test in 2012 for publication.
 - ✓ *Code will be made available to community.*
- *Parallel MECCA via MPI (message-passing interface)*: Completed for
 - ✓ MPI-based *contour integration of KKR Green’s functions*: 1/3 less CPU.
 - ✓ MPI-based KKR TF-QMR *sparse-matrix iterative solves*: Student delayed testing at ORNL due to move of collaborator to PNNL. Ongoing in 2012.
 - ✓ MPI-based parallel k-space integration: Software engineering ongoing.

Physics Improvements for Accurate and Faster 10^6 Atom Simulations

All these new and unique algorithms permit large-scale simulations in $O(N)$ time while avoiding previous computational bottlenecks in other DFT codes!

- *Optimal Basis-set Representation via Saddle-points in Charge-density*: Developed, tested, and published a fast site-centered, optimal spherical harmonic basis-set expansion determined *a priori* by location of saddle-points in the local total density.
 - ✓ Accurate, small basis sets to facilitate 10^6 atom simulations, with a reduction in basis by factor of 2 to 3!
 - ✓ Rapid estimate of starting potentials and charge-densities for generic alloys.
 - ✓ For disordered alloys, resolved long-standing disagreement between Coherent-Potential Approximation (CPA), Special Quasi-random Structures (SQS), and Cluster Expansion (CE) approximations.
 - ✓ More reliable applications for plasma, such as for NIF equation of state.

Publications:

- Aftab Alam and D.D. Johnson, Phys. Rev. B **80**, 125123-12 (2009).
- Aftab Alam, Brent Kraccek, and D.D. Johnson, Phys. Rev. B **82**, 024435-16 (2010).
- B. G. Wilson, D. D. Johnson, and Aftab Alam, High Energy Density Physics 7, 61-70 (2011).

- *Isoparametric Integration over Convex, Site(Atom)-dependent, Voronoi Polyhedra (VP)*: For general physics application that use VP or MECCA’s need for physics-based VP for 10^6 -atom simulations, we developed weighted-VP integration method with weights determined from radii associated with the saddle-points in the local electronic density.
 - ✓ Up to **10^5 faster and 10^7 more accurate** than some popular methods. Only ~2 milliseconds are needed for each face of VP. For 1000 atoms we need approximately 18 sec of additional time over ASA-based MECCA.
 - ✓ Code made available to the community.
 - ✓ Permits elimination of ASA approximation in electronic-structure codes.

Publication:

- Aftab Alam, S. N. Khan, Brian G. Wilson, D. D. Johnson, Phys. Rev. B **84**, 045105-11 (2011).
- Aftab Alam and D. D. Johnson, Phys. Rev. B **85**, 144202-8 (2012).

- ***Accurate and Fast Numerical Solution of Poisson's Equation:*** We developed, tested, and published a fast site-centered solution of Poisson's Equation. Importantly, this novel solution required the developments in the previous bullets, i.e., physics-based VP and integration over VP using isoparametric integrations.
 - ✓ No ill-convergent multipole methods are needed.
 - ✓ No FFTs are required, eliminating a bottleneck for large-scale simulations!
 - ✓ Works for all site-centered methods.
 - ✓

Publication:

- Aftab Alam, Brian G. Wilson, and D. D. Johnson, Phys. Rev. B **84**, 205106-8 (2011).

2. Numerical Results and Discussion

Some MECCA and Novel Methods Applications to Materials

A. Disordered, Partially Ordered and Fully Ordered (Meta)Stable Phases in Alloys

In aerospace materials aluminium-lithium is a prototype alloy that is the basis of aircraft skin. Until this work, no one has successfully compared disordered, partially ordered, and fully ordered metastable and stable phases that reproduce the observations, especially off-stoichiometric L_{12} -ordered precipitate phase. We have successfully and directly done so, for the first time, using the algorithms discussed above implemented in MECCA.

B. Effects of Processing Temperature on Properties of Co-Pt-type Permanent Magnets

Most L_{10} CoPt-type magnetic alloys, such as CoPt, FePd, and FePt, exhibit strong magnetocrystalline anisotropy and have applications as permanent magnets, with properties controlled by the presence of planar structural defects created during thermal processing that act as the dominant pinning centers in these materials.

With the improvements in MECCA, we can directly predict (unique to MECCA)

- Curie Temperature: MECCA 724 K, with 720 K experimentally.
- Order-Disorder: MECCA 1056 K, with 1100 K experimentally.

Each estimate is within a few percent, and still only $L=0$ for potential and charge density in the total energy calculation and via ASA integrations.

C. Generalized Solid-State Nudged-Elastic Band

A proper solid-state nudged elastic band (G-SSNEB) method was developed to determine reaction pathways of solid–solid transformations involving both atomic and unit-cell degrees of freedom. We combine atomic and cell degrees of freedom into a unified description of the crystal structure so that calculated reaction paths are insensitive to the choice of periodic cell. For the Rock-salt–to–Wurtzite transition in CdSe, we demonstrated that the method is robust for mechanisms dominated either by atomic motion or by unit-cell deformation. Notably, the lowest-energy G-SSNEB

mechanism found changes with cell size from a concerted transformation of the cell coordinates in small cells to a nucleation event in large cells.

D. Liquid-metal-induced fracture mode of Martensitic T91 Steels

The liquid–metal-induced fracture mode of T91 martensitic steel was investigated via TEM and theory. Contrary to previous claims of quasi-cleavage fracture, the dominant fracture mode is intergranular cracking at martensite laths and prior austenite grain boundaries. These fracture mode results clarify an outstanding issue in liquid–metal embrittlement of steels that generally occur in a heavily deformed microstructure. Several cracks were arrested at intergranular carbides, suggesting a metallurgical strategy for impeding liquid–metal-induced crack propagation.

E. Analysis of nonequilibrium HCP precipitate growth in FCC matrices

An analytical analysis was made of HCP precipitate growth and applied to Ag-Al alloys that show rapid precipitation during cooling, which is Ag-rich HCP precipitate inside Al-rich matrix phase. Results from ordered and disordered Ag-Al and the wetting of solute at planar stacking faults, as well as interphase boundaries between Al and AlAg precipitate phase, were calculated to assess quantities needed in the aspect ratio rate formula. Precipitate aspect ratio versus growth time was compared to TEM results.

Publications (this period)

*NOTE: From work initially supported on this grant, some papers were completed after moving to Ames Laboratory and Iowa State University, from seed funding from DOE and Ames Laboratory. These are included in “**Joint Funding by DOE**”.

Sole Funding by DOE-BES and this grant (¶), except for computational support

1. ¶Aftab Alam, Brent Kraccek, and D.D. Johnson, "Structural, Magnetic and Defect Properties of Co-Pt-type Magnetic-Storage Alloys: density-functional theory study of thermal processing effects," Phys. Rev. B **82**, 024435-16 (2010). [10.1103/PhysRevB.82.024435](https://doi.org/10.1103/PhysRevB.82.024435)
*Selected for 16 August 2010 issue of Virtual Journal of Nanoscale Science & Technology
<http://www.vjnano.org>.
2. ¶ Daniel Finkenstadt and D.D. Johnson, "Interfacial Energies of HCP precipitates in FCC matrices: A density-functional theory study in Al-Ag", Phys. Rev. B **81**, 014113-9 (2010).
[10.1103/PhysRevB.81.014113](https://doi.org/10.1103/PhysRevB.81.014113)
3. ¶Daniel Finkenstadt and D.D. Johnson, "Analysis of nonequilibrium HCP precipitate growth in FCC matrices: application to Al-Ag" Materials Science & Engineering A **525** (1-2) 174-180 (2009). DOI: [10.1016/j.msea.2009.07.004](https://doi.org/10.1016/j.msea.2009.07.004)

Joint Funding by DOE (and this grant (¶)) and Other Federal and Non-Federal Sources

4. ¶D. Sheppard, P. Xiao, W. Chemelewski,† D. D. Johnson, and Graeme Henkelman, "A generalized solid-state nudged-elastic-band method," J. of Chem. Phys. **136**, 074103-8 (2012). [http://dx.doi.org/10.1063/1.3684549](https://dx.doi.org/10.1063/1.3684549).
5. ¶Aftab Alam and D. D. Johnson, "Structural Properties and Relative Stability of (Meta)Stable Ordered, Partially-ordered and Disordered Al-Li Alloy Phases," Phys. Rev. B **85**, 144202-8 (2012). [http://dx.doi.org/10.1103/PhysRevB.85.144202](https://dx.doi.org/10.1103/PhysRevB.85.144202)
6. ¶M. L. Martin, T. Auger, D. D. Johnson, I. M. Robertson, "Liquid-metal-induced fracture mode of Martensitic T91 steels," J. of Nuclear Materials **426** (1-3), 71-77 (2012).
[http://dx.doi.org/10.1016/j.jnucmat.2012.03.040](https://dx.doi.org/10.1016/j.jnucmat.2012.03.040)
7. ¶B. G. Wilson, D. D. Johnson, and Aftab Alam, "Multi-center electronic-structure calculations for plasma equation of state," High Energy Density Physics 7 (Issue 2), 61-70 (2011).
[10.1016/j.hedp.2011.01.002](https://doi.org/10.1016/j.hedp.2011.01.002)
8. ¶Aftab Alam, S. N. Khan, Brian G. Wilson, D. D. Johnson, "Efficient Isoparametric Integration over arbitrary, space-filling Voronoi polyhedra for electronic-structure calculations," Phys. Rev. B **84**, 045105-11 (2011). [http://dx.doi.org/10.1103/PhysRevB.84.045105](https://dx.doi.org/10.1103/PhysRevB.84.045105)
9. Lin-Lin Wang and D. D. Johnson, "Ternary Tetradymite Compounds as Topological Insulators," Phys. Rev. B **83**, 241309(R) (2011).
[http://dx.doi.org/10.1103/PhysRevB.83.241309](https://dx.doi.org/10.1103/PhysRevB.83.241309)
10. Anant D. Kulkarni, Lin-Lin Wang, Duane D. Johnson, David Sholl, Karl Johnson, "First-Principles Characterization of Amorphous Phases of MB₁₂H₁₂, M=Mg, Ca," J. Phys. Chem. C **114**, 14601-14605 (2010). [10.1021/jp101326g](https://doi.org/10.1021/jp101326g)

11. L.-L. Wang, Dennis Graham, I.M. Robertson, and D.D. Johnson, "On the reversibility of hydrogen-storage reactions in $\text{Ca}(\text{BH}_4)_2$: characterization via experiment and theory," J. Phys. Chem. C **113** (46), 20088-20096 (2009). [10.1021/jp906660v](https://doi.org/10.1021/jp906660v)
12. ¶ Aftab Alam and D.D. Johnson, "Optimal site-centered electronic-structure basis set from a displaced-center expansion: Improved results via *a priori* estimates of saddle-points in the density" Phys. Rev. B **80**, 125123-12 (2009). [10.1103/PhysRevB.80.125123](https://doi.org/10.1103/PhysRevB.80.125123)
13. ¶ J.B. Liu and D.D. Johnson, "bcc-to-hcp Transformation Pathways in Iron versus Hydrostatic Pressure: Coupled Shuffle and Shear Modes," Phys. Rev. B **79** (13), 134113-9 (2009). <http://dx.doi.org/10.1103/PhysRevB.79.134113>
14. ¶ H. I. Li, K. Pussi, K. J. Hanna, L.-L. Wang, D. D. Johnson, H.-P. Cheng, H. Shin, S. Curtarolo, W. Moritz, J. A. Smerdon, R. McGrath, and R. D. Diehl, "Surface Geometry of C_{60} on Ag(111)," Phys. Rev. Lett. **103**, 056101-4 (2009). DOI:10.1103/PhysRevLett.103.056101
*Selected as Viewpoint in Physics [Physics 2, 64 (2009)]. *Selected as PRL Cover Art.
15. ¶ M. Dadfarnia, P. Novak, D.C. Ahn, J.B. Liu, P. Sofronis, D.D. Johnson, and I.M. Robertson, "Recent Advances in the Study of Structural Materials Compatibility with Hydrogen", Advanced Materials **22**(10), 1128-1125 (2010). [10.1002/adma.200904354](https://doi.org/10.1002/adma.200904354)
16. ¶ L.-L. Wang and D. D. Johnson, "Predicted Trends of Core-Shell Preferences for 132 Late Transition-Metal Binary Alloyed Nanoparticles" J. Amer. Chem. Soc. **131**, 14023-29 (2009). [10.1021/ja903247x](https://doi.org/10.1021/ja903247x)
17. ¶ S. Kibey, L.-L. Wang, J. B. Liu, H.T. Johnson, H. Sehitoglu, and D. D. Johnson, "Prediction of twinning stresses in fcc alloys: application to Cu-Al alloys" Phys. Rev. B. **79**, 214202 (2009). DOI: [10.1103/PhysRevB.79.214202](https://doi.org/10.1103/PhysRevB.79.214202)

Sole Funding by other Federal and Non-Federal Sources

18. Z. Zhang, L. Li, L.-L. Wang, S. I. Sanchez, Q. Wang, D. D. Johnson, A. I. Frenkel, R. G. Nuzzo, J. C. Yang, "The Role of $\gamma\text{-Al}_2\text{O}_3$ Single Crystal Support to Pt Nanoparticles Construction," Microscopy and Microanalysis **17** (S2), 1324 (2011).
19. L. Li, Z. Zhang, J. Ciston, E. A. Stach, L.-L. Wang, D. D. Johnson, Q. Wang, A. I. Frenkel, S. I. Sanchez, M. W. Small, R. G. Nuzzo, J. C. Yang, " H_2 -driven crystallization of supported Pt nanoparticles observed with aberration-corrected Environmental TEM," Microscopy and Microanalysis **17** (S2), 1604 (2011).
20. Brent Kraczek, Scott Miller, R.B. Haber, and D.D. Johnson, "Adaptive spacetime method using Riemann jump conditions for coupled atomistic-continuum dynamics," J. Comp. Phys. **229**, 2061-2092 (2010). [10.1016/j.jcp.2009.11.023](https://doi.org/10.1016/j.jcp.2009.11.023)
21. Scott Miller, Brent Kraczek, R.B. Haber, and D.D. Johnson, "Multi-field, spacetime discontinuous Galerkin methods for linearized elastodynamics," Comput. Methods in Appl. Mech. and Engrg. **199**, 34-47 (2009). [10.1016/j.cma.2009.09.012](https://doi.org/10.1016/j.cma.2009.09.012)
22. Teck L. Tan and D.D. Johnson, "Topologically correct phase boundaries and transition temperatures for Ising Hamiltonian via self-consistent coarse-grained cluster-lattice models," Phys. Rev. B **83**, 144427-12 (2011). <http://dx.doi.org/10.1103/PhysRevB.83.144427>
23. Zhongfan Zhang, et al., "Preparation and Characterization of Pt/ $\gamma\text{-Al}_2\text{O}_3$ Model Catalyst on NiAl Alloy," Microscopy & Microanalysis **16**, 1464-1465 (2010).

Lin-Lin Wang and D. D. Johnson, "Hydrogen Desorption from Ti-doped MgH₂(110) Surfaces: Catalytic effect on reaction pathways and kinetic barriers," J. of Phys. Chem. C **116**, 7874–7878 (2012). <http://dx.doi.org/10.1021/jp300794x>

Aftab Alam and D. D. Johnson, "Chemically Mediated Quantum Criticality in NbFe₂," Phys. Rev. Lett. **107**, 206401-5 (2011). [10.1103/PhysRevLett.107.206401](http://dx.doi.org/10.1103/PhysRevLett.107.206401).

People

Principle Investigator: Duane D. Johnson

Post-Doctoral Researchers:

Aftab Alam (*partial support*)

Graduate Student Research Assistants:

Suffian Khan (U.S. citizen, partial support on grant, then ORNL 2009 HERE fellowship, followed by EFRC through the Center for Defect Physics at ORNL).

Teck Tan (graduated 2010)

Academics and Computer/Database Administrator:

Dan Finkenstadt (U.S. citizen, graduated, now Professor U.S. Naval Academy)

Database: Andy Loftus (before 2011, 5% support for care of Structural Database)

Database: Dora Cai (before 2011, database support, mostly from NCSA)

✓ Plan to resurrect database at Ames Laboratory/Iowa State University in 2012.

DOE Interactions related to this Award (no support from this grant):

Brian Wilson, LLNL (Equation of State Group).

Bill Shelton, PNNL (EMSL)

Leveraging Activities

- LLNL has helped fund (with small partial student support) the Voronoi polyhedral integration area, along with some extension to MECCA for extreme high-T applications. The MECCA code has been shared with LLNL through Brian Wilson (Equation of State Group).

Updated List of Support

D.D. Johnson

2/1/07 - 1/31/10 DOE/BES \$585,000 (NO COST EXTENSION, move to Ames)

A Thermodynamic Density-Functional Theory and High-Performance Code for Complex Materials with up to Multi-Million-Atom Unit Cells

D.D. Johnson

9/16/07 - 9/15/10 NSF/DMR/CMMT \$376,374 (NO COST EXTENSION, ending 9/12)

Ab Initio Prediction of Properties of Complex Solids Having Short-Range Order and Partial Long-Range Order

Ralph Nuzzo (PI), J. Yang, A. Frenkel, and D.D. Johnson

9/15/09 – 9/14/12 DOE/BES-catalysis \$1,051,083

The Reactivity and Structural Dynamics of Supported Metal Nanoclusters Using Electron Microscopy, In-situ X-ray Spectroscopy, Electronic Structure Theories, and Molecular Dynamics Simulations

I. Robertson (PI), D.D. Johnson, J. Zuo (NO COST EXTENSION)

12/31/05 - 2/26/10 DOE (Sandia Metal-Hydride Center of Excellence) \$1,250,000

Metal Hydride-Based Hydrogen Storage

H. Sehitoglu and D.D. Johnson (NO COST EXTENSION – received no funds)

6/1/08 - 5/31/11 NSF/metals \$330,970

Twinning Studies via Experiments and DFT-Mesoscale Formulation

(G.M. Stocks, Oak Ridge National Laboratory (DOE/EFRC Prime)

10/01/09 – 09/30/14 \$3.8M/year

EFRC: Student supported through Illinois (\$54 K/year)

Post-doc partially supported (\$30K/year)

Bill McCallum, Ames Laboratory

1/3/12 – 12/31/14 (18 month + possible 18 month renewal) \$2.2M/3 years

ARPA-E: Novel high-energy permanent magnet without critical elements

Jun Cai, PNNL

1/3/12 – 12/31/14 (18 month + possible 18 month renewal) \$2.4M/3 years

ARPA-E: Manganese-based Permanent Magnet with 40 MGOe at 200C.

D.D. Johnson (Ames Lab) and Brian Wilson (LLNL)

10/2/12 – 9/30/15 \$380K/year

FES: Electronic-Structure of Warm Dense Matter via Multicenter Green's Function Techniques