

Augmented Basis Sets in Finite Cluster DFT

Jim Davenport

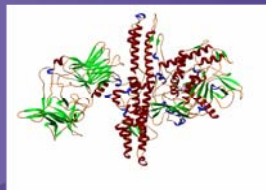
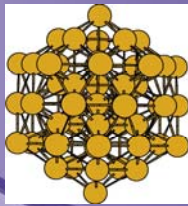
*Computational Science Center
Center for Functional NanoMaterials*

IMA/Minneapolis

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SIXTY YEARS
OF DISCOVERY
1947-2007

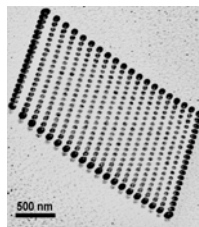


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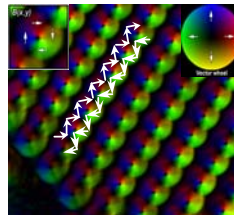
Office of
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U.S. DEPARTMENT OF ENERGY



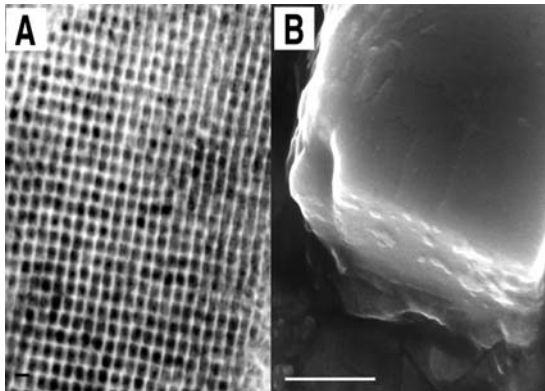
Nickel NanoDots Diameter ~ 5nm



Ni dots (M. Malec, BNL)



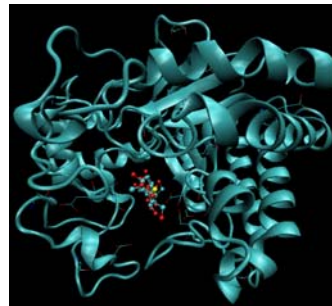
Magnetic inductance map (Y. Zhu, BNL)



Assembly of iron nanocubes $7 \times 7 \times 7 \text{ nm}^3$
 Dumestre et. al. Science 303, 821 (2004)

Cellulose Degrading Enzyme

- Cel6A
- Crystal structure (PDB - 1QK2)
- Acid proposed (Asp122)
- **Base uncertain** (ASP175, or ASP401)
- pKa shifts
- Simulations details:
 - GROMACS
 - solvated system $\approx 40\text{K}$ atoms
 - 10λ windows charging FE
 - 20λ windows ΔLJ FE
 - temp 300K, 2 fs timestep
 - reaction field
- Yolanda Small, J. Davenport



Density Functional Theory

In Practice: Obtain charge density and total energy via solutions single particle Schrodinger equations

$$\left\{ -\frac{1}{2} \nabla^2 + V(\vec{r}) \right\} \psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r})$$

$$V(\vec{r}) = \sum_{\vec{R}} -\frac{Z_{\vec{R}}}{|\vec{r} - \vec{R}|} + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + \mu_{xc}[\rho(\vec{r})]$$

DFT Solutions

- Basis Set → Eigenvalue Problem
 - Plane Waves
 - Gaussians $r^l \exp(-\alpha r^2) Y_{lm}(\theta, \phi)$
 - Slater type orbitals: $r^{n-1} \exp(-\zeta r) Y_{lm}(\theta, \phi)$
 - Augmented plane waves
 - spheres – (numerical s, p, d etc.) $Y_{lm}(\theta, \phi)$
 - interstitial – plane waves
- Need to solve Poisson
 - APW: $\rho \rightarrow$ pseudo ρ with same multipole moments
 - Gaussians → Coulomb integrals calculated

Augmented Methods

- APW - Slater
- Linear APW - O. K. Anderson, Koelling, others
- Linear Muffin Tin Orbitals, Anderson
- Full Potential LAPW (FLAPW)
 - Matheiss & Hamann, Weinert, others
- Highly Accurate Solutions
 - nodes, cusps at nuclei, forces are difficult
- Wien2k code
- Further Developments, Projector Augmented Wave Method (PAW), VASP Code
- Real Space version of PAW - Mortensen et. al. Phys Rev B **71** (2005).

LASTO

- **L**inear **A**ugmented **S**later **T**ype **O**rbital method
- Schrodinger equation in mixed basis set
 - numerical functions inside atom centered spheres
 - Slater type orbitals between spheres
- Scalar relativistic Dirac eq. inside
- Full Dirac for core levels
- Solve Poisson equation between spheres on numerical grid using smoothed charge densities
 - multigrid, hypre
- Solve Poisson Eq. inside spheres as Dirichlet problem
- K. S. Kang, J. Glimm, D. E. Keyes, and M. McGuigan

Inside Spheres

2 functions: solution at ϵ and its energy derivative

$$\phi_N(\vec{r}) = \sum_{\lambda\mu} \left\{ a_{N,j\lambda\mu} g_{j\lambda}(r_j) + b_{N,j\lambda\mu} \dot{g}_{j\lambda}(r_j) \right\} Y_{\lambda\mu}(\hat{r}_j)$$

spherical part of H:

$$\int_I \Phi_N H \Phi_N d^3r = \sum_{j,\lambda,\mu} \epsilon a_{N,j\lambda\mu} a_{N',j\lambda\mu} + a_{N,j\lambda\mu} b_{N',j\lambda\mu} + \epsilon b_{N,j\lambda\mu} b_{N',j\lambda\mu} \langle \dot{g}_{\lambda\mu} | \dot{g}_{\lambda\mu} \rangle$$

Outside the Spheres - Tails

Basis Set:

$$\phi_{nlm}(\vec{r}) = r^{n-1} \exp(-\zeta r) Y_{lm}(\vec{r})$$

Analytic Fourier Transforms

Addition Theorem:

$$\phi(\vec{r} - \vec{R}) = \sum_{L',L''} 4\pi I(L, L', L'') V_{nl'l''}(r, R) Y_{L'}(\vec{r}) Y_{L''}(\vec{R})$$

Use Rayleigh Expansion:

$$\exp(i\vec{q} \cdot \vec{r}) = \sum_{l,m} 4\pi i^l j_l(qr) Y_{lm}^*(\vec{q}) Y_{lm}(\vec{r})$$

Match sum of all tails at each sphere

Poisson Equation

- Rectangular grid
- Replace spherical average charge density inside spheres with a smooth pseudo-density
- interpolate onto grid
- Standard Poisson solvers
- Yields Coulomb potential outside, & on spheres
- Solve inside as Dirichlet problem

Poisson Equation

Density Inside: Spherical Harmonic Expansion

$$\tilde{\rho}(\vec{r}_j) = \sum_{\ell m} \tilde{\rho}_{\ell m}(r_j) Y_{\ell m}(\hat{r}_j)$$

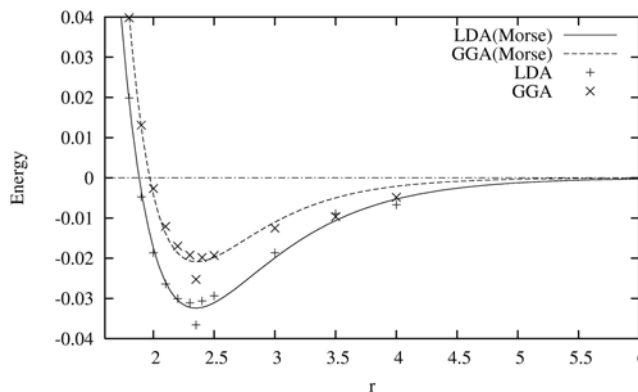
Pseudo Density Inside

$$\tilde{\rho}_{\ell m}(r_j) = \alpha_{\ell m} (r / R_j)^\ell \left[1 - (r / R_j)^2 \right]^n$$

Implementation

- Obtain Coulomb, exchange potentials from input density
- Expand site centered STO's about other sites via addition theorem
- Match smoothly onto numerical solutions inside spheres
- Construct Hamiltonian and overlap matrices
- Obtain eigenvalues, eigenvectors
- Charge density, total energy
- Partial occupancy - smearing ~ 1 mH

Palladium Dimer Binding Energy



Pd Clusters: Binding Energy

N	LASTO	NWChem
2	0.56 eV/atom	0.47 eV/atom
4	1.27 eV/atom	1.41 eV/atom
8	2.19 eV/atom	1.87 eV/atom

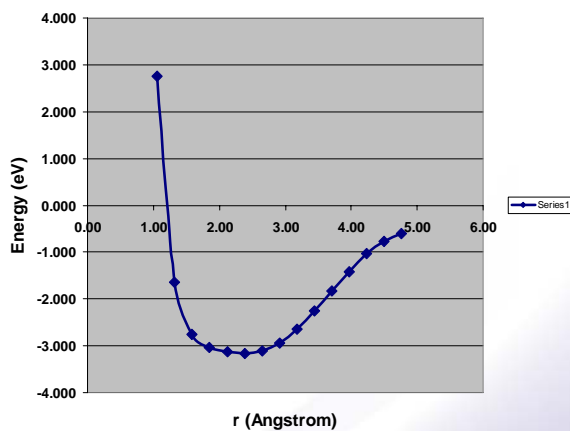
Summary of LASTO Experience

- Very Accurate - We Think
 - needs better tests
- Avoid supercells for finite clusters
- All electron, no pseudo potentials
- Code is Complex
- Spheres Lead to Discontinuities
- Hard to do Exact Exchange
- Want to Compare Gaussian Based Codes
- Especially How to Scale to Petaflops/Exaflops

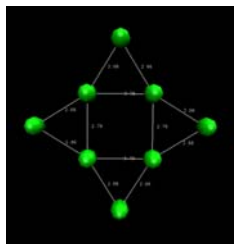
Gaussian Based Codes

- NWChem, GAMESS
- Gold, Palladium Clusters
- SBKJC Basis (Stevens, Basch, ...)
- Effective Core Potential
- Up to 2048 processors on Blue Gene/L @ BNL
- Current version scales to ~ 512 processors

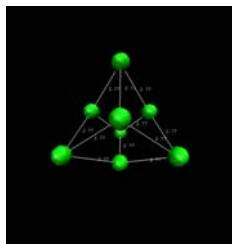
NWChem: Hydrogen/Palladium 13



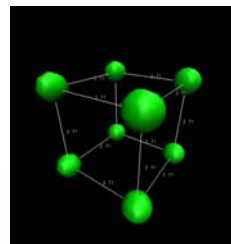
GAMESS: 8 Atom Gold Clusters



0.00 eV



0.53 eV



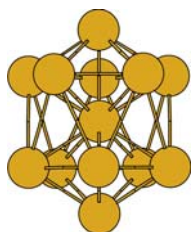
1.11 eV

close to bulk bond length, 2.88 Å

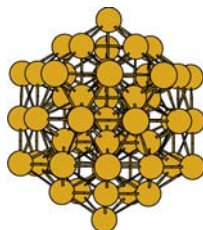
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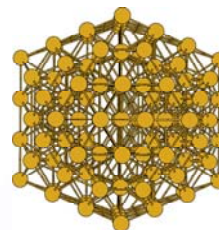
Gold Clusters - Icosahedral versus Octahedral Coordination



Au13



Au55



Au147

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Energetics - Au_N Clusters

N	O_h energy/atom	I_h energy/atom	ΔE E _{I_h} -E _{O_h}	L (bond length)
13	-1.93 eV	-1.73 eV	2.67 eV	2.78 Å
55	-3.09 eV	-3.12 eV	-1.66 eV	2.96 Å 2.52 Å

Conclusion

- Jury is out on Gaussian versus Numerical
- Need more studies on large systems
- 1000's of atoms, 10,000's processors
- **How Many Structures Exist?**
- DFT will ultimately rationalize our understanding of nanoclusters - similar to surfaces
- Thanks to Yolanda Small and Mike McGuigan @ BNL