Augmented Basis Sets in Finite Cluster DFT

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Nickel NanoDots Diameter ~ 5nm

Ni dots (M. Malec, BNL)  Magnetic inductance map (Y. Zhu, BNL)
Assembly of iron nanocubes 7x7x7 nm³

Cellulose Degrading Enzyme

- Cel6A
- Crystal structure (PDB - 1QK2)
- Acid proposed (Asp122)
- Base uncertain (ASP175, or ASP401)
- pKa shifts
- Simulations details:
  - GROMACS
  - solvated system ≈ 40K atoms
  - 10 λ windows charging FE
  - 20 λ 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

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

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

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 → pseudo rho 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 nucleii, forces are difficult
- Wien2k code
- Further Developments, Projector Augmented Wave Method (PAW), VASP Code

LASTO

- **Linear Augmented Slater Type Orbital 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 $\epsilon$ and its energy derivative

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

spherical part of $H$:

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

Outside the Spheres - Tails

Basis Set:

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

Analytic Fourier Transforms

Addition Theorem:

$$\phi(\tilde{r} - \tilde{R}) = \sum_{L, L'} 4\pi i (L, L', L'') V_{mL'}(r, R) Y_L(\tilde{r}) Y_{L'}(\tilde{R})$$

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

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

Pseudo Density Inside

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

<table>
<thead>
<tr>
<th>N</th>
<th>LASTO</th>
<th>NWChem</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.56 eV/atom</td>
<td>0.47 eV/atom</td>
</tr>
<tr>
<td>4</td>
<td>1.27 eV/atom</td>
<td>1.41 eV/atom</td>
</tr>
<tr>
<td>8</td>
<td>2.19 eV/atom</td>
<td>1.87 eV/atom</td>
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</tbody>
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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

![Graph showing energy (eV) vs. r (Angstrom) for 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
Energetics - $\text{Au}_N$ Clusters

<table>
<thead>
<tr>
<th>$N$</th>
<th>$E_{Oh}$ energy/atom</th>
<th>$E_{Ih}$ energy/atom</th>
<th>$\Delta E$ $E_{Ih} - E_{Oh}$</th>
<th>$L$ (bond length)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>-1.93 eV</td>
<td>-1.73 eV</td>
<td>2.67 eV</td>
<td>2.78 Å</td>
</tr>
<tr>
<td>55</td>
<td>-3.09 eV</td>
<td>-3.12 eV</td>
<td>-1.66 eV</td>
<td>2.96 Å 2.52 Å</td>
</tr>
</tbody>
</table>

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