A DFT++ Code with Evolutionary Optimization Technique

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Atomistic Modeling - Zabaras

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Context and Motivation

- DFT++ is an alternate formulation of density functional theory in which the Kohn-Sham equations are expressed as an optimization problem
- This optimization step is the most computationally expensive part of the approach.
- In an attempt to accelerate convergence, we will perform the necessary optimizations using a genetic algorithm

DFT++ Formalism

- A Lagrangian reformulation of the Kohn-Sham equations.

$$L_{\mathrm{LDA}(\psi_i(r),\phi(r))} = -\frac{1}{2}\sum_i f_i \int \mathrm{d}^3 r \psi_i^*(r)\nabla^2\psi_i(r) \quad (1)$$

$$+ \int \mathrm{d}^3 r V_{\mathrm{ion}(r)n(r)+\int \mathrm{d}^3 r \epsilon_{\mathrm{xc}(n(r))n(r)}} \quad (2)$$

$$- \int \mathrm{d}^3 r \phi(r)(n(r)-n_0) - \frac{1}{8\pi}\int \mathrm{d}^3 r ||\vec{\nabla}\phi(r)||^2 \quad (3)$$

- Minimizing the variation of the Lagrangian with respect to ψ_i and ϕ will recover the Kohn-Sham and Poisson equations
- We can explicitly calculate the energy and its gradients

DFT++ Equations

If n is the electronic density coefficients with respect to our basis,

$$L_{\mathrm{LDA}(C,\phi)} = -\frac{1}{2}\mathrm{Tr}(FC^\dagger LC) + (Jn)^\dagger(V_{\mathrm{ion}+OJ\epsilon_{\mathrm{xc}(N)-O\phi)+\frac{1}{8\pi}\phi^\dagger L\phi} \quad (4)$$

$$\frac{\partial L_{\mathrm{LDA}}}{\partial Y^\dagger} = (I - OCC^\dagger)HCFVU^{-1/2} + OCVQ(V^\dagger[\tilde{H}, F]V) \quad (5)$$

$$\frac{\partial L_{\mathrm{LDA}}}{\partial \phi^\dagger} = -\frac{1}{2}OJn + \frac{1}{8\pi}L\phi \quad (6)$$

with

$$H = -\frac{1}{2}L + I^\dagger(\mathrm{Diag}\,V_{\mathrm{sp})I} \quad (7)$$

$$\tilde{H} = C^\dagger HC \quad (8)$$

DFT++ Algorithm

1. Calculate the ionic potential $(V_{\text{ion}})_\alpha = \int b^*_\alpha(R) V_{\text{ion}(R)\text{d}^3 r}$ where $(V_{\text{ion}})_\alpha$ represents the overlap of the ionic potential with each basis function.
2. Choose initial wavefunctions W randomly and make them orthonormal with $Y = WU^{-1/2}$ where U is the matrix of wave function overlaps.
3. Optimize the wavefunction Y until the energy is converged. For example, if we are using the steepest-descent optimization algorithm, this may involve:
   1. Calculate the energy as described below.
   2. Calculate the gradient of the energy with respect to the wavefunction.
   3. Take a step down the gradient G of the energy with $Y_n = Y_{n-1} - \lambda G$

   where λ is some step size.

DFT++ Energy Calculation

1. Calculate the overlap matrix $U = W^\dagger O W$.
2. Calculate the orthonormal wavefunctions $Y = WU^{-1/2}$.
3. Calculate the charge density with $n = f \ \mathrm{diag}((IC)(IC)^\dagger)$ where f is orbital occupancy.
4. Calculate the vector expansion coefficients of the electrostatic potential by solving the Poisson equation: $\hat{\phi} = -4\pi L^{-1} OJn$.
5. Finally, calculate the energy by

$$E = -\frac{1}{2} f \mathrm{Trace}(W^\dagger LWU^{-1}) + \tilde{V}^\dagger n + \frac{1}{2} n^\dagger J^\dagger O \hat{\phi} + n^\dagger J^\dagger OJ\epsilon_{\mathrm{xc}n} \quad (9)$$

Evolutionary optimization

- A powerful optimization strategy based on natural evolution
- Successive "generations" of solutions are considered
- The best solutions in one generation are used to guess trial solutions in the next
- Example: crystal structure prediction

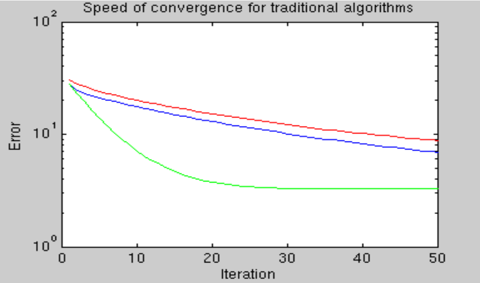
Our genetic algorithm

1. Choose random initial population. Evaluate the energy and fitness of each organism.
2. Create the new child generation:
    1. Promote some number of the best solutions from the previous generation to the new one.
    2. Create the rest of the child solutions using the crossover operation described below. For each new solution created this way, two distinct parent solutions are selected based on their own fitnesses.
    3. Evaluate the energy and fitness of each new solution.
3. Set (child population) $\rightarrow$ (parent population) and go to 2.

Results

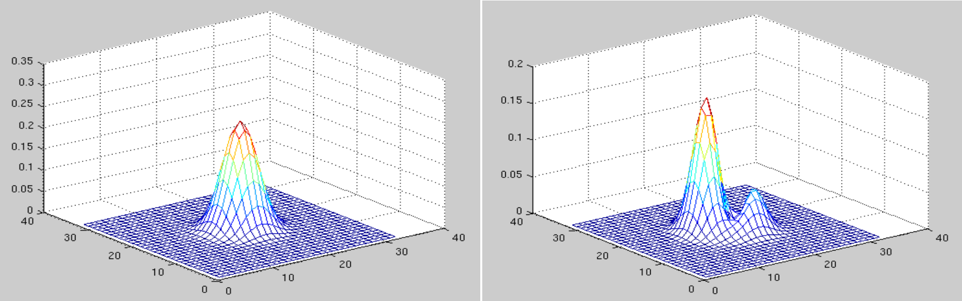
- The genetic algorithm fails to perform for understandable reasons
  - Does not optimally exploit the problem's partial spatial separability
  - Does not efficiently sample phase space or introduce new genetic information
- Luckily, we have the traditional optimization algorithms to fall back on!

Traditional algorithms: convergence

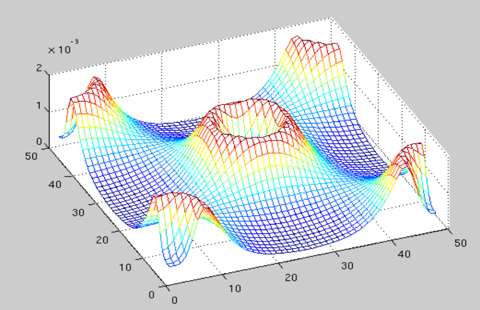


- Red: Steepest-descent
- Blue: Conjugate-gradient
- Green: Preconditioned CG

Hydrogen atom



Ge FCC solid



- (100) cross-section of Ge solid
- Diamond lattice
- 8 atom conventional cell
- Starkloff-Joannopoulos PP

Summary

- Explored the DFT++ formalism
- Implemented a functioning DFT++ code with several optimizers
- Explored genetic algorithms
- Implemented a genetic algorithm and understood why it failed
- Did some interesting calculations anyway