8th. World Congress on Computational Mechanics (WCCM8)
5th European Congress on Computational Methods in Applied Sciences and Engineering (ECCOMAS 2008)
June 30 –July 5, 2008
Venice, Italy

Numerical Algorithms for Solving Nonlinear Eigenvalue Problems in Quantum Mechanical Calculations

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Key Words: *Nonlinear eigenvalue problems, Quantum mechanical calculation, Kohn-Sham equations, Self-consistent field iteration*

ABSTRACT

We will discuss numerical algorithms for solving discretized Kohn-Sham equations. This type of problems arises from electronic structure calculation which is nowadays an essential tool for studying the microscopic quantum mechanical properties of molecules, solids and other nanoscale materials. Through the density functional theory (DFT) formalism, one can reduce the many-body Schrödinger equation, which is a linear eigenvalue problem, used to describe the electron-electron and electron-nucleus interactions to a set of single-electron equations that have far fewer degrees of freedom. However, the price one has to pay is to solve a nonlinear eigenvalue problem in which the matrix Hamiltonian is a function of the desired but unknown eigenvectors to be computed. Currently, the most widely used numerical algorithm for solving this type of problem is the Self-consistent field (SCF) iteration. The algorithm can be viewed as a fixed point iteration in which approximations to the eigenvectors of a fixed Hamiltonian are computed at each iteration, and these eigenvectors are used to update the Hamiltonian for the next iteration. However, it is well known that the simplest form the SCF iteration often fails to converge to the correct solution. We will present an analysis of the SCF iteration that shows the conditions under which the SCF iteration forms a contraction mapping on the space of electron charge densities. If these conditions are satisfied, the SCF iteration is guaranteed to converge to the correct solution. We will discuss various strategies for improving the convergence of SCF when such conditions are violated. An alternative algorithm that is designed to minimize the total energy of the atomistic system of interest directly will also be presented. In this algorithm, the total energy of the system is minimized in a sequence of overlapping subspaces. The minimizer within each subspace is obtained by applying an enhanced SCF iteration to a projected nonlinear eigenvalue problem. We will demonstrate how this algorithm can be used to compute the electronic structures of both molecules and solids. Techniques for overcoming convergence difficulties in metallic systems will also be discussed.

REFERENCES

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