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3D Pseudospectral Self-Consistent Field Approximation

Thomas Kerkhoven and Wing Chow and Franklin Bodine

Department of Computer Science
University of Illinois at Urbana-Champaign, 1304 W. Springfield Ave.,Urbana, IL 61801, U.S.A.
Phone: +217-333-6726, Fax: +217-333-3501,
E-mail: kerkhoven@cs.uiuc.edu, chow@ceg.uiuc.edu

1. Introduction

A novel three-dimensional computational procedure is presented for the determination of the self-consistent electronic structure in the electrostatic field due to the nuclei. The model includes an eigenvalue problem for Schrödinger's equation coupled with Poisson's equation for the electrostatic potential. The solution is expanded in Fourier plane waves $\phi_k(x)$ in a manner similar to that utilized in the somewhat related Car-Parrinello method [5]. These waves are characterized by the wave vector k and the equations are approximated by a pseudospectral projection that employs real space collocation and the Fast Fourier Transform (FFT).

2. Self-Consistent Field Approximation

Due to electron-electron interactions Schrödinger's equation for a many electron system is not separable and does not facilitate a single electron description. Approximation of the system Hamiltonian by a sum of terms, each dependent on the coordinates of a single electron only, provides then separability of Schrödinger's equations and the ability to describe electrons in the system one at a time. The many electron Schrödinger equation is reduced to an equation for many single electrons by the well known Self-Consistent Field Approximation (SCF). This procedure provides us for the description of the steady state with the solution for many single electron eigenstates of Schrödinger's equation. In the latter the potential energy in the Hamiltonian is provided by an electrostatic part determined by the solution of Poisson's equation for the electrostatic potential plus an electron density dependent exchange-correlation term. Approximation of the many electron system by the SCF then amounts to self-consistent solution of this coupled system of equations. The inclusion of proper anti-symmetrization of the many-electron wave-function, provides the Hartree-Fock equations. This approximaiton includes as additional potential energy terms

both an exchange and a correlation term which is dependens on the electron density. The many electron system is then described as follows: Poisson's equation coupled with an eigenvalue problem for Schrödinger's equation

$$-\nabla \cdot [\epsilon \nabla \phi] = \rho,$$
$$-\frac{\hbar^2}{2} \nabla \cdot [\frac{1}{m} \nabla \psi_l] + [V - E_l]\psi_l = 0. \qquad (1)$$

The potential V in Schrödinger's equation is given by $V = -e\phi + V_{xc}(n)$. Here $V_{xc}(n)$ is the local exchange-correlation potential which depends on the electron density n [7]. For problem size N ($\gg K$) the best possible complexity equals the solution size $= K \times N$.
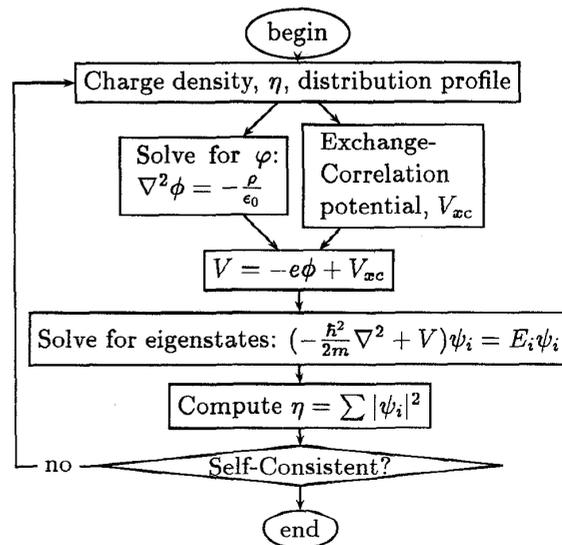

Fig. 1 Quantum Mechanical Electron Structure Simulation using SCF.

3. Pseudo-Spectral SCF

Let k indicate the wave-vector with Euclidean length k. Then, in pseudo-spectral space, Poisson's

equation (Ker = constants) can be represented as:

$$\tilde{\phi}_{\vec{k}} = \frac{1}{\epsilon_0 k^2} \tilde{\rho}_{\vec{k}}$$

The symmetry of the Hamiltonian in Schrödinger's equation (1) indicates that the energy eigenstates will be real. The Fourier transforms that figure in the pseudospectral projection are indicated by the orthogonal transformation Q for the forward FFT with inverse Q^T for the backward transformation. In spectral space this provides for Schrödinger's equation the representation:

$$\left(\frac{\hbar^2}{2m} D_{k^2} + Q^T D_V Q \right) \tilde{\psi} = E\tilde{\psi}.$$

As usual, in this formula $\hbar$ is the reduced Planck's constant and m is the electron mass. The symmetry of the Schrödinger Hamiltonian remains evident after Fourier transformation to spectral space. This eigenvalue problem for Schrödinger's equation is discretized by truncation of the Fourier series expansion of the solution at a suitable maximal kinetic energy $K_{\max} \boxminus |\mathbf{k}|_{\max}^2 / 2m$.

In a typical simulation the total sought after number of eigenstates, K, is much smaller than the total number of plane waves $N = n_x n_y n_z$. With $\alpha = x, y, z$, the Fourier transform restricts n_α to values $n_\alpha = 2^{l_\alpha}$ and for periodic problems of length L_α in the α-direction the wave numbers $k_\alpha = \frac{2\pi}{L_\alpha} j_\alpha$.

Depending on the maximal energy resolution, the number of plane waves N can exceed the number of electron states K by a factor of 100 or more. These relevant eigenstates are located at the low end of the energy spectrum and their distribution depends strongly on the configuration of the atomic nuclei. Degeneracies of m ($\approx$ 10, say) electron states at one energy level are likely to be present in three-dimensional models. The eigenvalue solver was, therefore, designed to be sufficiently robust that it can accurately resolve the energy spectrum also if the energy states are highly concentrated in certain energy ranges.
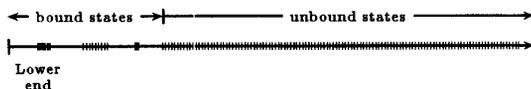

Fig. 2 Typical eigenvalue distribution

The eigenvalue solver operates by the generation a set of vectors that may be expected to have large components in the direction of the sought subspace. Next, the eigenvalue problem is projected onto this set of vectors and the much smaller dimensional projected problem is solved by Arnoldi's method [1]. The explicit orthogonalization of eigenvectors that

is included in Arnoldi's method then provides for the orthogonality that is hard to realize otherwise within degenerate subspaces. The algorithm is designed such that the dimensionality k of the projected problem is adjusted locally in response to the observed eigenvalue concentration. In this manner costly global orthogonalization is circumvented and replaced by an adaptive algorithm.
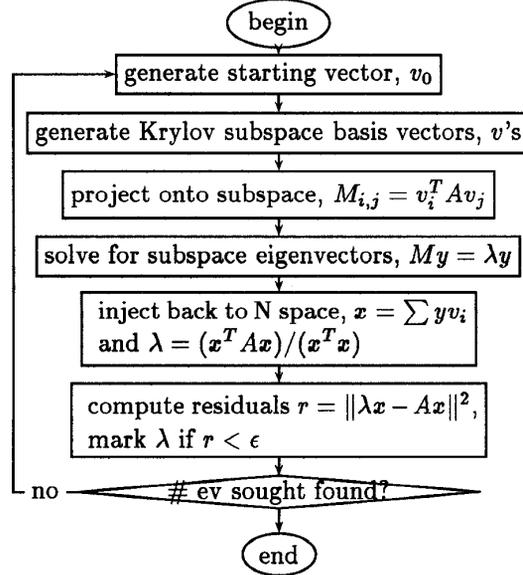

Fig. 3 Eigenvalue solver

Selection of desired ranges in the energy spectrum of the Hamiltonian is realized by the inversion of a quadratic expression of the Hamiltonian. The inversion here is implemented employing a Preconditioned Conjugate Gradient algorithm (PCG). For this particular method it can be shown that the iteration number is independent of the number of plane waves that is employed in the approximation.

4. Resolution of the Nuclei

The only singularities in the atomic SCF are due to the nuclei. In Poisson's equation the nuclei introduce point charge singularities. Because the Fourier expansion of these point charge singularities is constant in spectral space, they present an obstacle to the realization of the potentially rapid convergence features of the Fourier expansion. Therefore, Fourier expansion of the singular point-charge distributions of the nuclei is circumvented. Instead, in Poisson's equation for the electrostatic potential for the nuclei are substituted smooth radial functions centered at the location of the nuclei. The potential corresponding to the singular point charge of the nuclei minus the smoothed charge distributions is added to the potential computed from the regularized charge

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distribution afterwards. This procedure facilitates in particular the accurate positioning of nuclei off the uniformly distributed meshpoints employed for collocation by the FFT.

5. Iteration to Self-Consistency

Self-consistent solution of the Schrödinger-Poisson problem in the SCF is realized in an iterative procedure of successive substitution for the eigenvalue problem for Schrödinger's equation and Poisson's equation for the electrostatic potential. The reliable convergence of this procedure to a self-consistent system solution is stabilized and accelerated by the application of a Jacobian-free version of Newton's method implemented with the GMRES algorithm [6]. Because this non-linear GMRES (NL-GMR) algorithm implements a version of Newton's method, a sufficiently accurate initial guess to the system solution must be provided. The efficacy of NLGMR in the context of systems of nonlinear elliptic partial differential equations was demonstrated in [4]. It was successfully applied to two-dimensional Schrödinger-Poisson models in [2, 3].

6. Computational Complexity

The constant iteration number of the PCG inversion of the quadratic in the Hamiltonian indicates that the cost of the generation of a Krylov subspace of size k for Arnoldi's method equals a constant times the computational complexity of the application of the Hamiltonian operator times k. The inner products that realize the explicit orthogonalization of Arnoldi's method in the k-dimensional subspace contribute a computational complexity equal to the solution size, N, times $k^2/2$. once the projection has been achieved the computational complexity of the projected eigenvalue solution is negligible. The realization of self-consistency of the coupled Schrödinger-Poisson is achieved in a fixed number of successive substitution iterations. The total computational complexity for the resolution of K eigenstates therefore comes out at $O[KN \log(N) + kKN]$. This is essentially optimal if the superior approximation properties of the Fourier expansion are taken into account.

7. Natural Parallelizability

The Arnoldi preconditioner amplifies a limited range of the energy spectrum selectively. Thus, the energy spectrum can be partitioned into a number of segments, each being computed independently from the others in parallel (very coarse grain parallelism). Note that the communication cost is minimal: only at the start (spreading the data) and the end (collecting the result) of each call to the eigenvalue solver. Load imbalance is a possible problem.

Therefore, load balancing techniques need to be employed for further speedup.

8. Significant Results

A numerical code in which the described algorithms have been realized was applied to a number of simple molecules and solid state structures. Figures of computed approximations are included for a simulation of methane (CH_4), benzene (C_6H_6) and diamond.
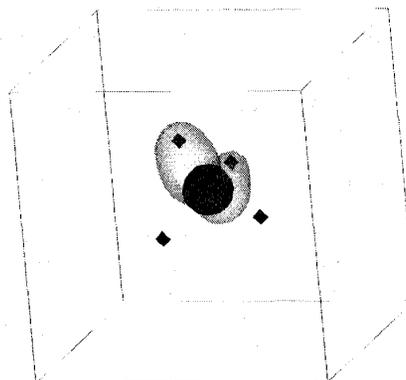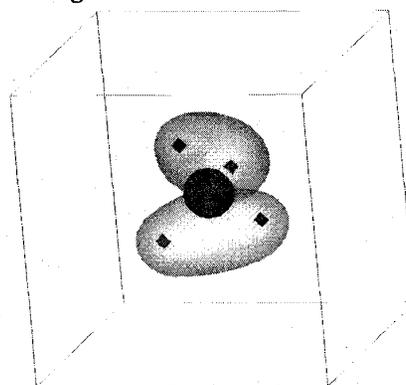

Fig. 4 2P orbital of methane.

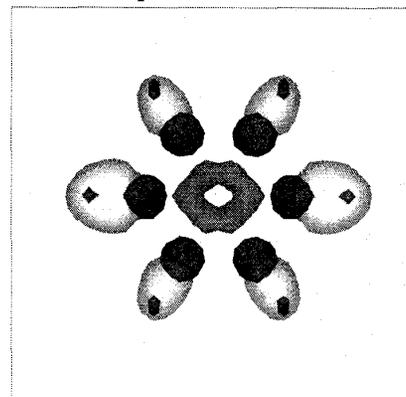Fig. 5 2P orbital of methane, degenerate with previous one.

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Fig. 6 π-orbital and electronic $C - H$ orbitals in benzene.
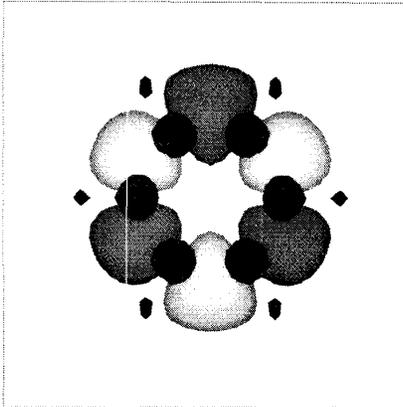

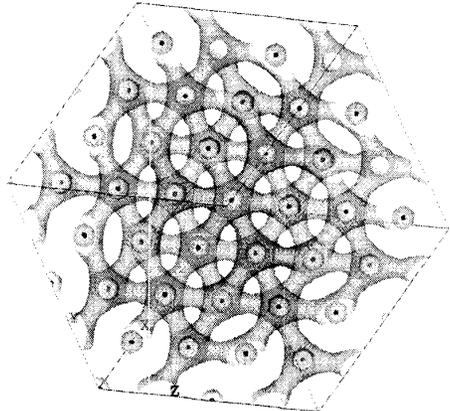Fig. 7 Electron-orbital reflecting molecular structure in benzene.

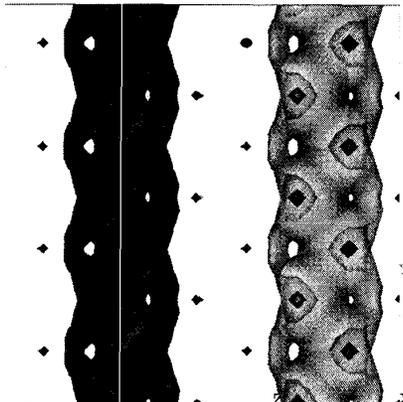Fig. 8 Multiple cell diamond simulation. 65-th electronic eigenstate, (1,1,1) direction.

Fig. 9 Multiple cell diamond simulation. 71-st

electronic eigenstate, plane Bloch wave.

9. Conclusions

A novel computational procedure was presented for the solution of the Schrödinger-Poisson system in the SFC. The computational complexity of the method for the computation of K electronic eigenstates in a plane wave expansion with N components equals $O[KN \log(N) + KN]$. The method was demonstrated in a collection of solid state and molecular structure simulations.

References

[1] W.E. Arnoldi. The Principle Of Minimized Iteration In The solution Of The Matrix Eigenvalue Problem. *Quart. Appl. Math.*, 9:17–29, 1951.

[2] T. Kerkhoven, A. T. Galick, U. Ravaioli, J. H. Arends, and Y. Saad. Efficient Numerical Simulation Of Two Dimensional Quantum Wells. *J. Appl. Phys.*, 68(7):3461–3469, October 1990.

[3] T. Kerkhoven, M. Raschke, and U. Ravaioli. Self-Consistent Simulation Of Quantum Wires In Periodic Heterostructure Structures. *J. Appl. Phys.*, pages 1199–1204, July 1993.

[4] T. Kerkhoven and Y. Saad. On Acceleration Methods For Coupled Nonlinear Elliptic Systems. *Numer. Math.*, 60(4):525–548, 1992.

[5] R.Car and M. Parrinello. . *Phys. Rev. Lett.*, 55:2471, 1985.

[6] Youcef Saad and Martin H. Schultz. GMRES: A Generalized Minimal Residual Method for solving Nonsymmetric Linear Systems. *SIAM J. Sci. Comput.*, 7:856–869, 1986.

[7] Frank Stern and Sankar Das Sarma. Electron Levels in GaAs $-$ Ga$_{1-x}$Al$_x$As Heterojunctions. *Physical Review B*, 30(2):840–848, 1984.