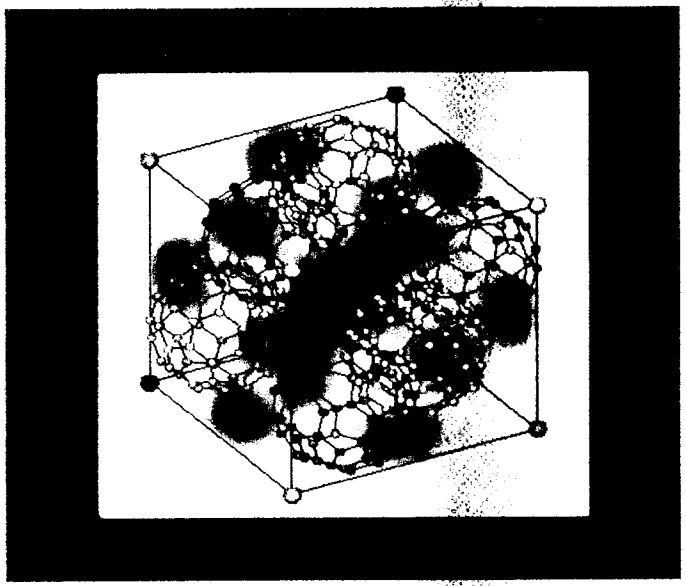
A Finite-Element Approach to Large-Scale Electronic Structure Calculations



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This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48

IPAM, UCLA, April 2002

Outline

- Motivation for the Finite Element Approach
- Construction of FE Basis Functions
- Boundary Conditions
- Solution of Schrodinger Equation
- Solution of Poisson's Equation
- Applications to Positron Annihilation
- Future Plans

Motivation

- The Finite Element (FE) method is widely used to solve differential equations in engineering applications.
- A vast base of literature, experience, algorithms and code is available.
- Numerically intensive steps rely on well-optimized sparse matrix methods.
- FE approach is well suited for massively parallel applications and exhibits favorable scalability for large systems.

Finite Elements offer an arbitrarily accurate and systematically improvable basis, like plane waves.

- Can treat larger systems in $O(N^3)$ method
- Offers a convenient strictly-local basis for O(N) methods

The Finite-Element Method Combines Significant Advantages of Grid-Based and Basis-Oriented Approaches

Plane-Wave Expansion Methods

- ***Variational***
- ***Systematically improvable basis set***
- Extended basis functions => dense matrices
- FFTs – parallelization difficult and poor scalability with system size
- Same resolution at all points in space

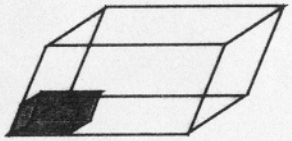
Finite Difference Methods

- Non-variational
- No systematic way to improve result
- ***Strictly local => sparse matrices***
- ***No FFTs – readily parallelizable and highly scalable with system size***
- ***Real-space resolution can be varied***

Finite Element Method

- ***Variational***
- ***Systematically improvable basis set***
- ***Strictly local basis functions => sparse matrices***
- ***No FFTs – readily parallelizable and highly scalable with system size***
- ***Real-space resolution can be varied***

The Finite Element Approach



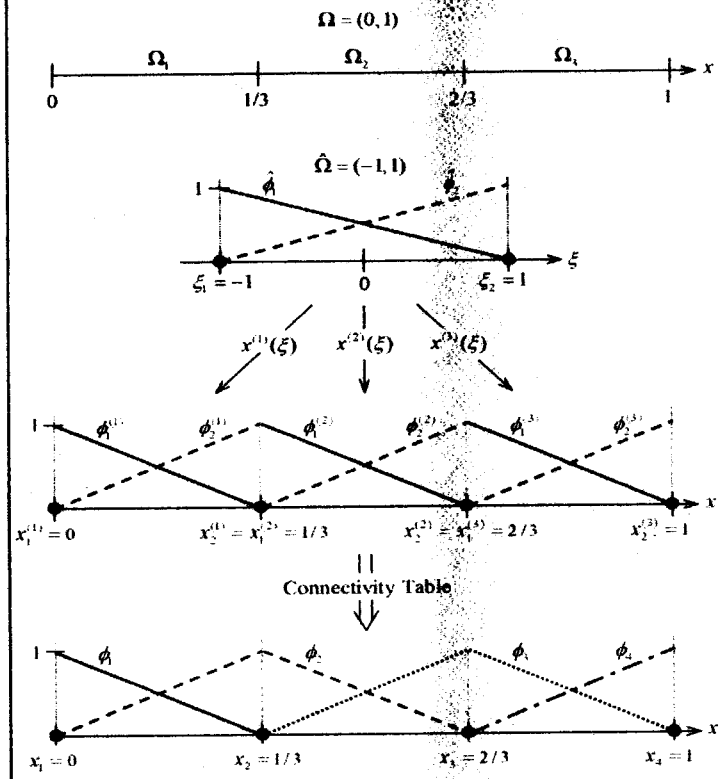
1. Break up the system into elements
2. Define polynomial functions within each element
3. Create strictly-local FE basis functions from these polynomial functions
4. Solve differential equation by expanding the solution in FE basis functions
   - Schrodinger equation => Sparse generalized eigenvalue problem
   - Poisson's equation => Sparse system of linear equations

We are using a variational formulation in which the FE basis set can be systematically improved by:

- Increasing the order (and number) of the basis functions
- Increasing the number of elements

Finite-Element Basis

Construction of 1-D piecewise-linear FE basis.



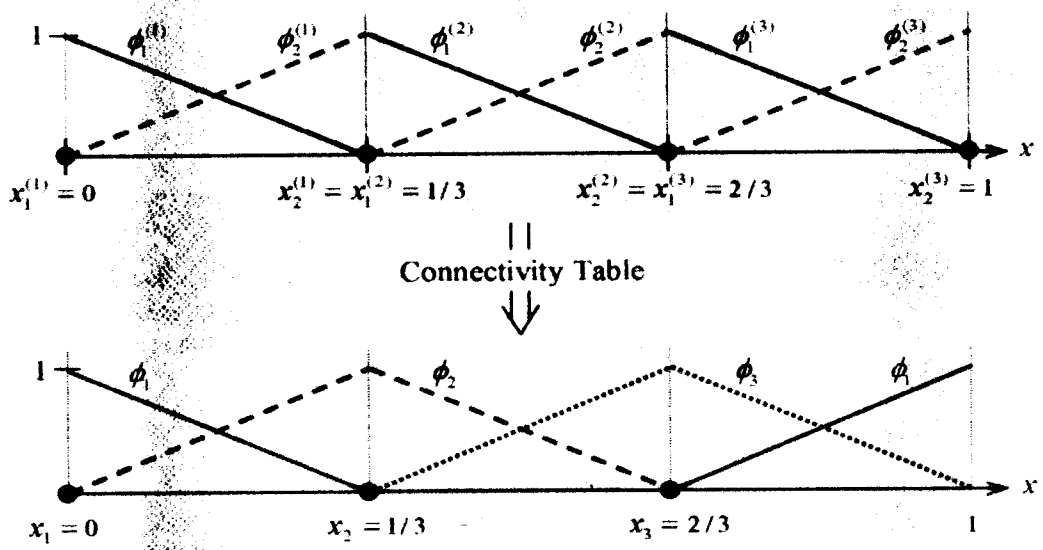
- Domain and *elements*.
- *Parent element* and basis functions.
- *Local basis functions* generated by transformations of parent basis function to each element.
- Final (global) piecewise-linear basis functions generated by piecing together local functions across inter-element boundaries.

→ **Strictly local, piecewise-polynomial basis.**

Value-Periodic Basis Functions

Construction of value-periodic piecewise-linear finite-element basis:

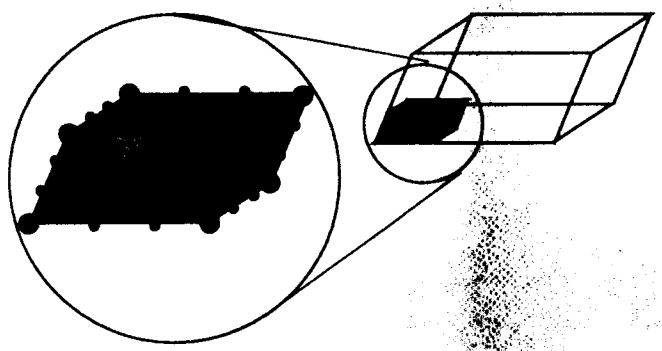
Piece together local functions across domain boundary as well as inter-element boundaries



Zero-value Dirichlet boundary conditions are introduced similarly by excluding basis functions that are non-zero on the boundary

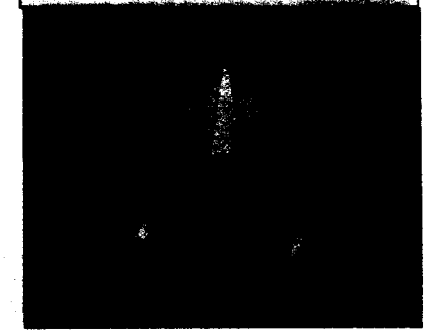
Finite Element Basis Functions in 3-D

- Divide the unit cell into elements.
- Define polynomial functions on each element.
  - 32 polynomials are specified by their values at 8 vertices and 24 edge nodes
  - each polynomial has value of 1.0 on one node and 0.0 on all others
  - this polynomial set is complete to cubic order – higher orders are possible
- Link polynomial functions at nodes on element boundaries to form FE basis functions
- 1 FE basis function per node; 7 FE basis functions per element for periodic BCs



Local polynomial function on vertex

FE basis function on vertex



FE basis functions are strictly localized over at most 8 neighboring elements

=> H and S matrices have at most 135 non-zero elements per row - sparse

The FE Basis Functions Have a Number of Interesting Properties

FE Basis functions are:

- Polynomial – general and systematically improvable
- Strictly local – well suited to large-scale calculations
- Value-periodic – continuous at boundary, but not necessarily differentiable at boundary
- C^0 – continuous, but not necessarily differentiable

FE basis function on vertex

C^0 basis offers additional flexibility over C^∞ bases (e.g. plane waves)

- C^0 basis can describe the wavefunction cusp at the nucleus
- C^0 basis includes all the more highly differentiable bases

But:

- Differential equations must be reformulated to work with C^0 bases

Schrodinger Solution: Basis Set Discretization

- To find an approximate solution, restrict u and v to a finite dimensional subspace $\mathbf{V}_n \subset \mathbf{V}$:

$$\text{Let } u = \sum_j c_j \phi_j \text{ and } v = \sum_i d_i \phi_i ,$$

where $\{\phi_k\}_{k=1}^n$ is a real FE basis satisfying the value BC and $\{c_j\}$ and $\{d_i\}$ are complex coefficients.

- Substitution of the above expansions into the weak formulation yields a generalized eigenproblem for the approximate eigenvalues ε and eigenfunctions $u = \sum c_j \phi_j$ of the weak formulation and thus of the original problem:

$$\mathbf{Hc} = \varepsilon \mathbf{Sc},$$

where

$$H_{ij} = \int_\Omega [\nabla \phi_i \cdot \nabla \phi_j - 2i\mathbf{k} \cdot \phi_i \nabla \phi_j + (V + k^2)\phi_i \phi_j] d\Omega$$

and

$$S_{ij} = \int_\Omega \phi_i \phi_j \, d\Omega .$$

- **Expansion in FE basis → sparse, generalized eigenproblem for desired eigenvalues and eigenfunction coefficients.**

Schrodinger Solution: Weak Formulation

- Take inner product with arbitrary test function v to form equivalent integral equation:

$$\int_\Omega v^*[-\nabla^2 u - 2i\mathbf{k}\cdot\nabla u + (V + k^2 - \varepsilon)u]d\Omega = 0$$

- Integrate by parts to reduce order of derivative and create boundary term:

$$\int_\Omega \nabla v^* \cdot \nabla u \, d\Omega - \int_\Gamma v^* \nabla u \cdot \hat{\mathbf{n}} \, d\Gamma + \int_\Omega v^*[-2i\mathbf{k}\cdot\nabla u + (V + k^2 - \varepsilon)u]d\Omega = 0$$

- Restrict v to satisfy value BC to reduce boundary term to

$$\sum_l \int_{\Gamma_l} v^*(\mathbf{x})[\nabla u(\mathbf{x}) - \nabla u(\mathbf{x} + \mathbf{R}_l)] \cdot \hat{\mathbf{n}} \, d\Gamma \quad \forall v \in \mathbf{V}$$

  (where **V** = subspace satisfying value BC)

- Substitute derivative BC to incorporate it:

$$\int_\Omega \nabla v^* \cdot \nabla u \, d\Omega + \int_\Omega v^*[-2i\mathbf{k}\cdot\nabla u + (V + k^2 - \varepsilon)u]d\Omega = 0 \quad \forall v \in \mathbf{V}$$

  Satisfaction of this Eq. is equivalent to satisfaction of differential Eq. *and* derivative BC

- The differential formulation is thus equivalent to the following *weak formulation*:

  Find scalars ε and functions $u \in \mathbf{V}$ such that

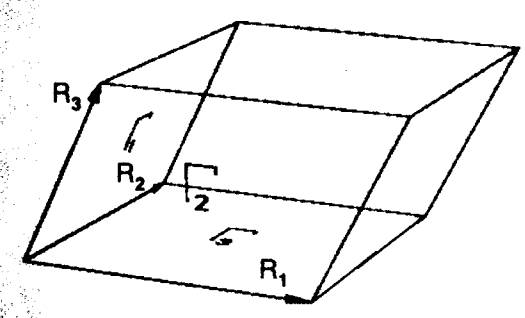
$$\int_\Omega \nabla v^* \cdot \nabla u \, d\Omega + \int_\Omega v^*[-2i\mathbf{k}\cdot\nabla u + (V + k^2 - \varepsilon)u]d\Omega = 0 \quad \forall v \in \mathbf{V}$$

- **Laplacian eliminated, derivative BC built in.**

Schrodinger Solution: Differential Formulation

Solve: $-\nabla^2\psi + V\psi - \varepsilon\psi = 0$

in parallelepiped cell with periodic potential V.



V periodic $\Rightarrow$ $\psi = ue^{i\mathbf{k}\cdot\mathbf{x}}, \quad u(\mathbf{x}) = u(\mathbf{x}+\mathbf{R})$

Differential formulation with value and derivative boundary conditions:

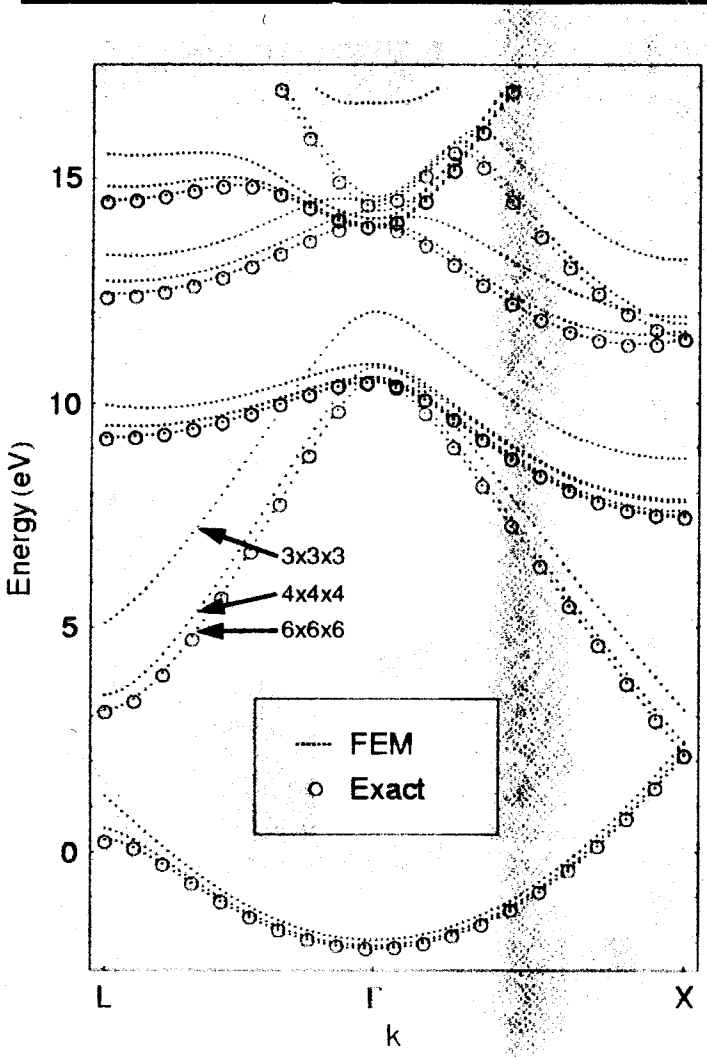
$$-\nabla^2 u - 2i\mathbf{k}\cdot\nabla u + \left(V + k^2 - \varepsilon\right)u = 0$$

$$\left.\begin{aligned} u(\mathbf{x}) &= u(\mathbf{x}+\mathbf{R}_l) \\ \hat{\mathbf{n}}\cdot\nabla u(\mathbf{x}) &= \hat{\mathbf{n}}\cdot\nabla u(\mathbf{x}+\mathbf{R}_l) \end{aligned}\right\} \forall \mathbf{x}\in\Gamma_l,\ l = 1,2,3$$

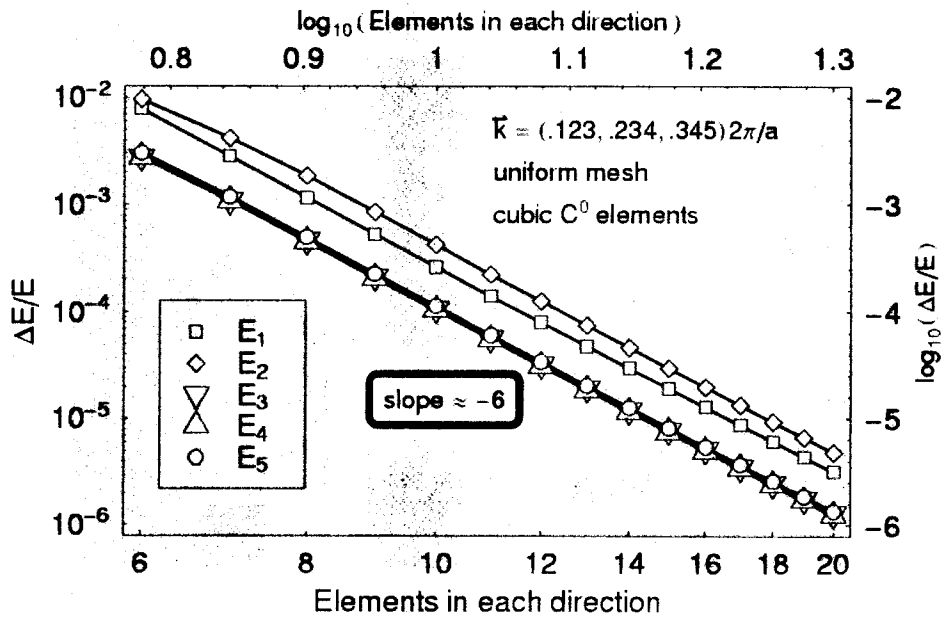
Basis is C^0 – how is ∇^2 operator treated?
Basis does not satisfy derivative boundary condition.

} Reformulate in weak form

Solutions to the Schrodinger Equation Converge Variationally



FE and exact band structures for Si pseudopotential, for a series of meshes.

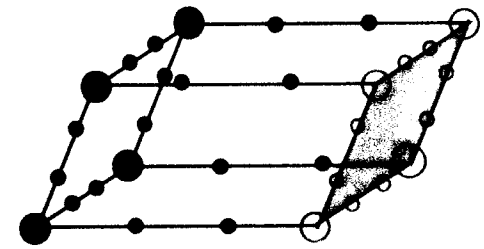


Relative error in first few FE eigenvalues for Si pseudopotential vs. number of elements in each direction.

- **Rapid, consistent, and variational convergence.**
- **Slope ≈ –6 ⇒ relative error of O(h^6),** where h = mesh spacing: **optimal theoretical order.**

The FE Method Readily Treats A Variety Of Boundary Conditions

- Dirichlet – impose value boundary condition on boundary basis functions
  - e.g. $\psi=0$ on boundary $\Rightarrow$ delete boundary basis functions



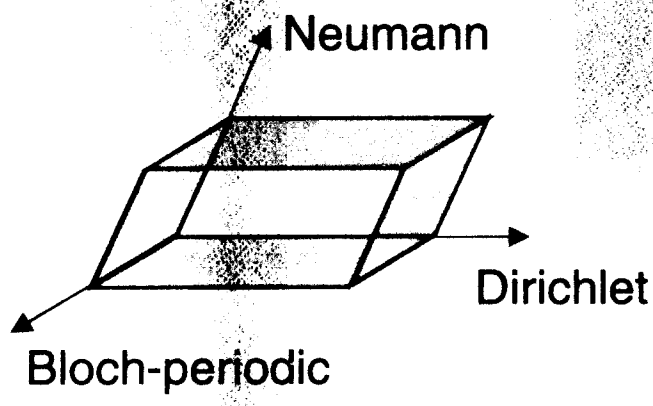
- Neumann – incorporate derivative boundary condition into weak formulation:

$$\int_{\Omega}\nabla v^{*}\cdot\nabla u\,d\Omega-\int_{\Gamma}v^{*}\nabla u\cdot\hat{\mathbf{n}}d\Gamma+\int_{\Omega}v^{*}\left[-2i\mathbf{k}\cdot\nabla u+\left(V+k^{2}-\varepsilon\right)u\right]d\Omega=0$$

  - ↳ =0 for zero-value Neumann boundary conditions

- Bloch-periodic
  - impose value periodic condition on the basis functions, like Dirichlet
  - incorporate derivative boundary condition into weak formulation, like Neumann

FE Calculations Can Handle A Variety Of Boundary Conditions



Positron distribution on a plane through a dislocation dipole in Cu. Each dislocation has split into two partials

Lower dimensional systems:

- Surfaces and Interfaces
- Dislocations
- Polymer chains

Assessing Convergence With System Size:

- Zero-value Dirichlet: wavefunction localized too rapidly
- Zero-derivative Neumann: wavefunction too extended

Poisson Solution: Similar Procedure

Differential formulation

$$-\nabla^2 V = f \quad \text{in } \Omega,$$

$$V(\mathbf{x}) = V(\mathbf{x} + \mathbf{R}_l) \quad \forall \mathbf{x} \in \Gamma_l,\ l = 1, 2, 3,$$

and

$$\hat{\mathbf{n}} \cdot \nabla V(\mathbf{x}) = \hat{\mathbf{n}} \cdot \nabla V(\mathbf{x} + \mathbf{R}_l)$$
$$\forall \mathbf{x} \in \Gamma_l,\ l = 1, 2, 3,$$

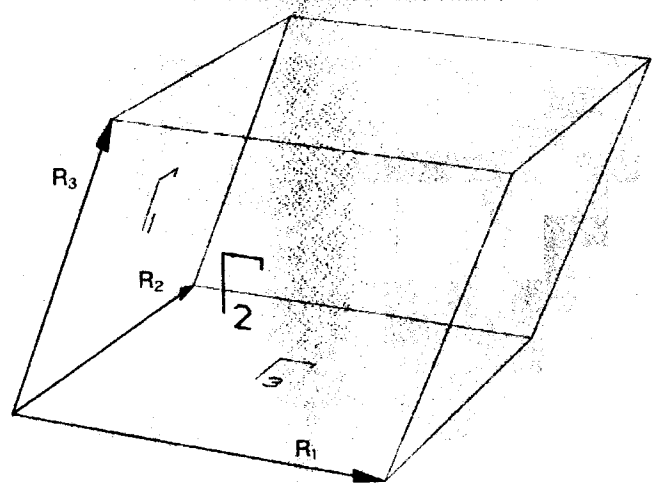
Weak formulation

Find $V \in \mathcal{V}$ such that

$$\int_\Omega \nabla v \cdot \nabla V \, d\Omega = \int_\Omega v f \, d\Omega \quad \forall v \in \mathcal{V},$$

where $\mathcal{V} = \{v:\ v(\mathbf{x}) = v(\mathbf{x} + \mathbf{R}_l)\ \forall \mathbf{x} \in \Gamma_l\}$.

- **Laplacian eliminated.**
- **Derivative BC built in.**



Parallelepiped unit cell.

Discretization

$$\mathbf{L}\mathbf{c} = \mathbf{f},$$

where

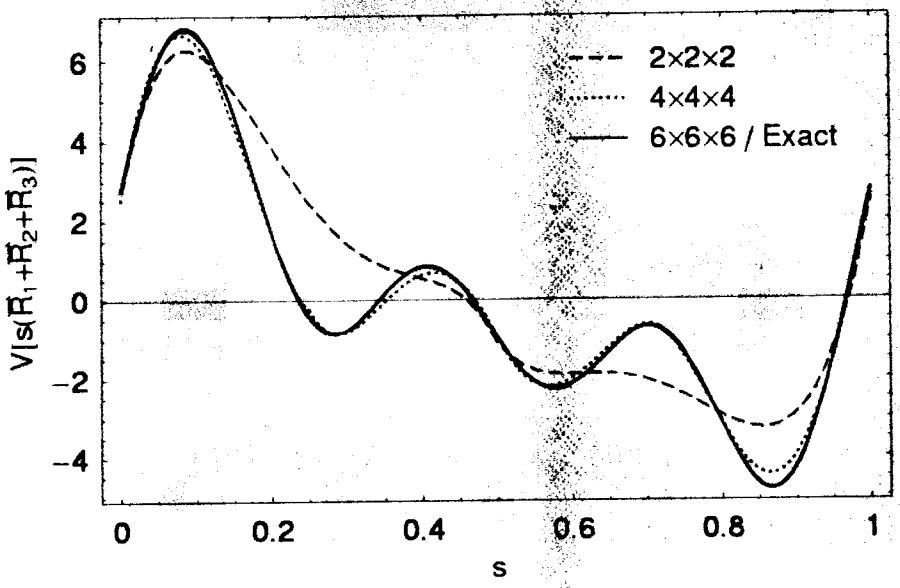
$$L_{ij} = \int_\Omega \nabla \phi_i \cdot \nabla \phi_j \, d\Omega$$

and

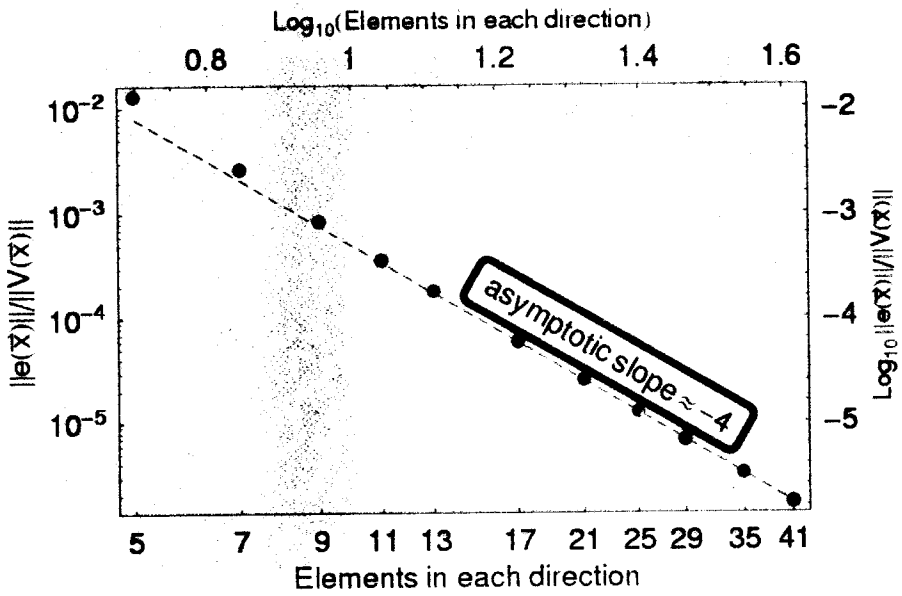
$$f_i = \int_\Omega \phi_i f \, d\Omega.$$

- **Expansion in FE basis → sparse, linear system for desired potential coefficients.**

Convergence of Poisson Solution



FE and exact solutions along diagonal of model triclinic cell, for a series of meshes.



Relative L^2 error in FE solution for model triclinic cell, for a series of meshes.

- **Convergence to smooth solution though basis is not smooth** (being merely C^0).
- **Convergence to derivative BC though basis does not satisfy it** (satisfying only the value BC).
- **Slope $\approx -4 \Rightarrow$ relative L^2 error of O(h^4),** where h = mesh spacing: **optimal theoretical order.**

Poisson Solution Scales Linearly with System Size

Iterations to convergence for a series of physically equivalent systems of increasing size based on model triclinic cell.

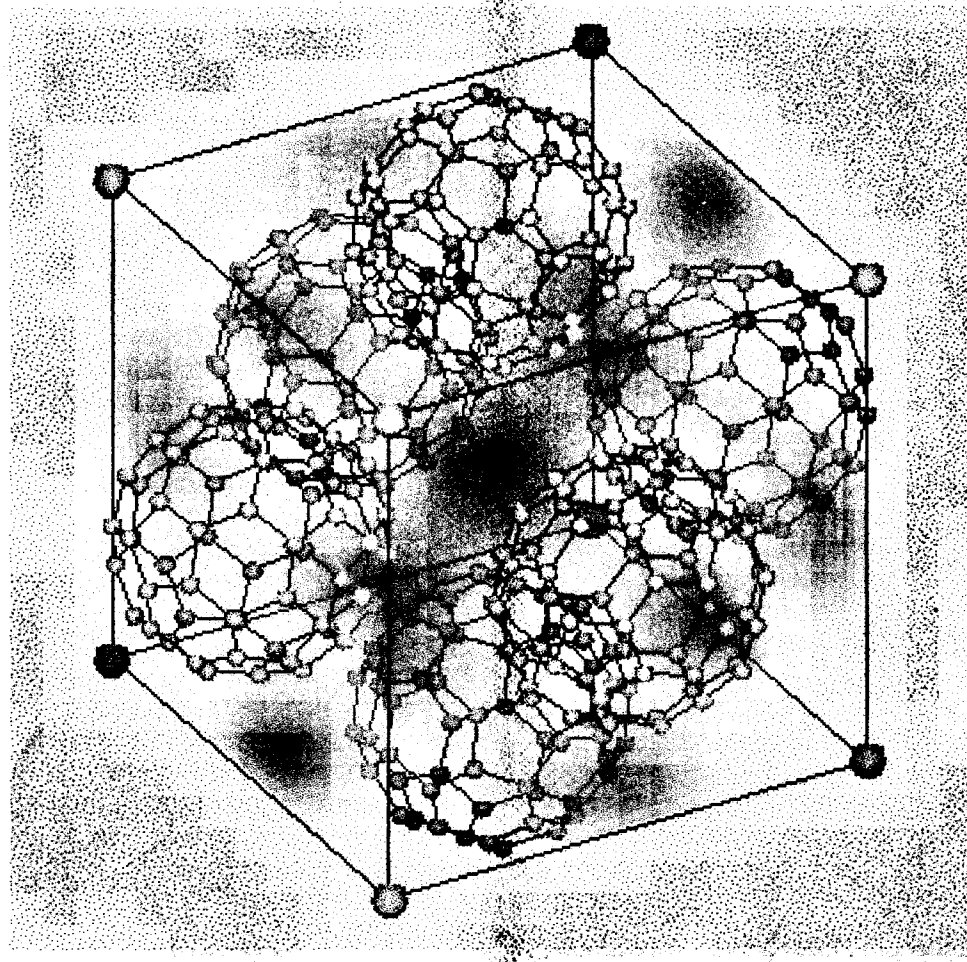
# Primitive cells in supercell	# Elements in each direction	L^2 error of solution, e_{L^2}	CG residual error, e_{CG}	CG iterations
1	10	5.39598E−4	5.20282E−6	48
2^3	20	5.39598E−4	5.22653E−6	48
3^3	30	5.39598E−4	5.18992E−6	48
4^3	40	5.39598E−4	5.22631E−6	48
5^3	50	5.39598E−4	5.26736E−6	48

- Iterations independent of system size.
- Operations per iteration increase linearly with system size.

⇒ **Total operations to solution scales linearly with system size.**

C_{60} Fullerenes - Large Open Structures

Positron charge density in Pa3 C_{60}
Only face-centered molecules shown.



Lifetimes for K_nC_{60} (ps)		
	FE	Puska-Nieminen
C_{60}	330	327
K_1C_{60}	273	276
K_3C_{60}	260	261

Positron sits mostly in octahedral sites in C_{60}

Current and Future Developments

Work in progress:

- Self-consistency and total energy capability
- Non-local pseudopotentials
- Optimization of numerical methods
    - Sparse generalized Hermitian eigensolver
    - Multigrid methods
- Parallelization

Future developments:

- Mixed basis approach
- Higher order elements

Our FE code is currently used to calculate positron distributions and lifetimes in materials to guide the interpretation of experimental data.

- The FE calculations accurately predict positron lifetimes for realistic defects
- Systems of over 5000 atoms have been successfully treated

Conclusions

The FE method offers an attractive approach for large-scale electronic structure calculations

- Combines advantages of basis-set approaches and real-space methods
- Well suited for massively parallel applications

Our FE code for electronic structure is under development

- Self-consistency and total energy calculations are the immediate goals

Current non-self-consistent applications to positron spectroscopy illustrate the power of this approach to treat systems of thousands of atoms