Electronic Structure of Condensed Matter
Fudan University - April 2010

Lecture 7: Iterative methods
Efficient Plane Wave and Grid Calculations
Molecular Dynamics with Forces from the Electrons

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Molecular Dynamics with Forces from the Electrons

OUTLINE

Brief outline of classical molecular dynamics (MD), relaxation of atom positions
- Methods for MD and for minimization

The Car-Parrinello advance
- Unified MD algorithm for nuclei and electrons
- "Fictitious dynamics" of the electrons – hard to use

General forms for iterative algorithms for K-S Eqs.
- Easier to understand than CP algorithm
- Algorithmic advances – iterative methods, FFT, . . .
- Expressions using plane waves

Examples
- Liquid carbon, Water, . . .

Classical Molecular Dynamics (MD)

Solve Newton's equations of motion for a complicated system

$$M_I \ddot{\mathbf{R}}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = \mathbf{F}_I[\{\mathbf{R}_J\}].$$

Verlet algorithm: advance position of each atom in time steps Δt

$$\mathbf{R}_I(t+\Delta t) = 2\mathbf{R}_I(t) + \mathbf{R}_I(t-\Delta t) + \frac{(\Delta t)^2}{M_I}\mathbf{F}_I[\{\mathbf{R}_J(t)\}], \qquad (18.2)$$

where the first two terms are just the law of inertia. The key property of the Verlet algorithm, well established in classical simulations, is that *the errors do not accumulate.* Despite the fact that the equations are only approximate for any finite Δt, the energy is conserved and the simulations are stable for long runs.

Typical MD uses forces derived from a force model – force F a simple function of positions of neighbors

Simulations with 100's, 1000's, 1,000,000's of atoms can describe liquids, solids at high temperature, phase transitions, diffusion, vibrational excitations, thermal behavior, solutions, disordered systems, ...

Typical calculation - many atoms in a cell with periodic boundary conditions

Relaxation of atomic positions to find stable structure

Do NOT want to conserve energy – want to lose energy as fast as possible to reach the lowest energy state

Simplest algorithm: Move atoms along the direction of the force by a magnitude proportional to the force. At sep n, move atoms to the positions at the next step, n+1

$$\mathbf{R}_I^{n+1} = \mathbf{R}_I^n + \alpha\, \mathbf{F}_I^n$$

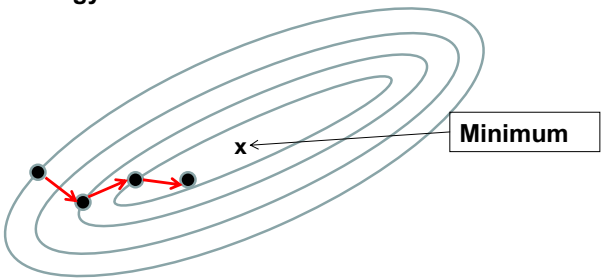
This is called "Steepest descent" because the coordinates are displaced along the direction of the gradient (F = - dE/dr)

In this algorithm the positions always move in the "downhill" direction.

Problems: As shown in the figure on the next slide, this can be very inefficient, walking back and forth toward the minimum – but never actually arriving at the minimum!

Steepest Descent

Energy contours around the minimum



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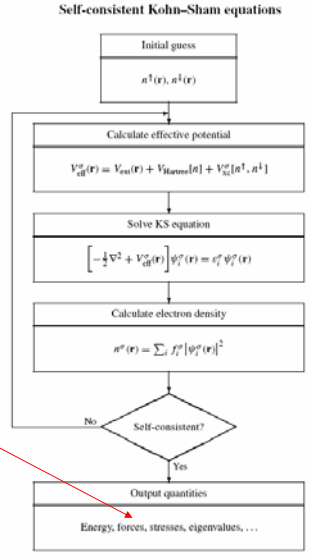
Usual approach to the Kohn-Sham problem

See Chapter 9 – Solving the Kohn-Sham Eqs.

Self-consistent Equations

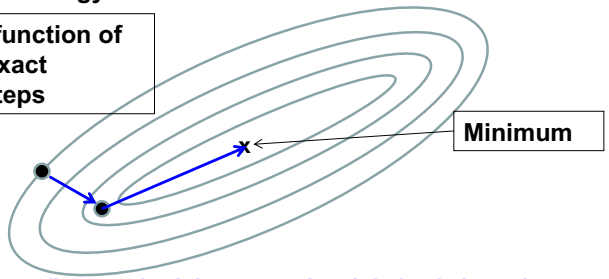
Solve equations with many cycles of iteration to get accurate solution - then calculate forces



Conjugate Gradients (CG)

Energy contours around the minimum

For quadratic function of 2 variables – exact solution in 2 steps



In the conjugate gradient method the energy is minimized along the direction of displacement – line minimization.

1. The first direction is along the gradient – same as steepest descent – except that one finds the minimum along that line.
2. The second direction is orthogonal – and there is a formula for following directions to be "conjugate" to all previous steps!

For a quadratic function of N variables, CG is guaranteed to reach the minimum in N steps. Very efficient for equations that are not quadratic

The textbook method for quantum mechanics -- Diagonalize Matrices

Two numerical problems:

1. Diagonalize matrix – find eigenvalues, vectors
2. Iterate to self-consistency – this is a minimization problem – minimize with respect to n(r)

Diagonalization – computer time scales as N_B^3

N_B^3 is size of basis

Efficient for small basis – LCAO, etc., for small problems

NOT efficient for large bases – Plane waves!

Iterate to self-consistency –

This is a minimization problem

Minimize total energy with respect to n(r)

(Recall - this is how the Kohn-Sham equations were derived!)

The iterations are a numerical way to reach the minimum

Can use Steepest Descent, Conjugate Gradient , . . .

"Ab initio" "First principles" Molecular Dynamics and Relaxation of the structure

Calculate forces from the electrons using the force theorem

$$E[\{\psi_i\},\{\mathbf{R}_I\}] = 2\sum_{i=1}^{N}\int \psi_i^*(\mathbf{r})\left(-\frac{1}{2}\nabla^2\right)\psi_i(\mathbf{r})d\mathbf{r} + U[n] + E_{II}[\{\mathbf{R}_I\}], \quad (18.3)$$

$$U[n] = \int d\mathbf{r}V_{\text{ext}}(\mathbf{r})n(\mathbf{r}) + \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\text{xc}}[n], \quad (18.4)$$

$$n(\mathbf{r}) = 2\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2, \quad (18.5)$$

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I}, \quad (18.6)$$

In principle, the Kohn-Sham approach gives exact forces

In practice, many examples show the forces are very accurate – tested by comparison with experiment in simple systems

The only problem – how to calculate forces on many atoms for thousands of time steps

The Car-Parrinello Advance

Summary

Of all the recent methods for computing the properties of materials from electronic equations, one stands out: i.e. the quantum molecular dynamics (QMD) simulations pioneered by Car and Parrinello in 1985 [156]. This work and subsequent developments have led to a revolution in the capabilities of theory to treat real, complex molecules, solids, and liquids including thermal motion (molecular dynamics), with the forces derived from the electrons treated by (quantum) density functional methods. Altogether, four advances create the new approach to electronic structure. These comprise:

- optimization methods (instead of variational equations),
- equations of motion (instead of matrix diagonalization),
- fast Fourier transforms (FFTs) – (instead of matrix operations), and
- a trace of occupied subspace (instead of eigenvector operations).

Car and Parrinello combined these features into one unified algorithm for electronic states, self-consistency, and nuclear movement. There has also been an explosion of alternative approaches that utilize the force theorem, together with efficient iterative methods described in App. M or simpler tight-binding-type methods. These are described in the present chapter as well as the Car–Parrinello method *per se*.

Treated briefly

The Car-Parrinello (CP) Algorithm

In the Car–Parrinello approach, the total Kohn–Sham energy is the potential energy as a function of the positions of the nuclei. Molecular dynamics for the nuclei using forces from this energy is the defining criterion for all forms of so-called "*ab initio* MD" using density functionals. *The special feature of the Car–Parrinello algorithm is that it also solves the quantum electronic problem using MD.* This is accomplished by adding a *fictitious* kinetic energy for the electronic states, which leads to a fictitious lagrangian for both nuclei and electrons [156][3]

$$\mathcal{L} = \sum_{i=1}^{N}\frac{1}{2}(2\mu)\int d\mathbf{r}|\dot{\psi}_i(\mathbf{r})|^2 + \sum_I \frac{1}{2}M_I\dot{\mathbf{R}}_I^2 - E[\{\psi_i\},\{\mathbf{R}_I\}] + \sum_{ij}\Lambda_{ij}\left[\int d\mathbf{r}\psi_i^*(\mathbf{r})\psi_j(\mathbf{r}) - \delta_{ij}\right].$$

Very clever! But hard to understand and to use – We will emphasize the other approaches that were stimulated by the CP work

The final term in (18.7) is essential for orthonormality of the electronic states. This lagrangian leads to MD equations for *both* classical ionic degrees of freedom $\{\mathbf{R}_I\}$ *and* electronic degrees of freedom, expressed as independent-particle Kohn–Sham orbitals $\psi_i(\mathbf{r})$.

Treated briefly

The Car-Parrinello Unified Equations of Motion

$$\mu\ddot{\psi}_i(\mathbf{r},t) = -\frac{\delta E}{\delta\psi_i^*(\mathbf{r})} + \sum_k \Lambda_{ik}\psi_k(\mathbf{r},t) = -H\psi_i(\mathbf{r},t) + \sum_k \Lambda_{ik}\psi_k(\mathbf{r},t), \quad (18.8)$$

$$M_I\ddot{\mathbf{R}}_I = \mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I}. \quad (18.9)$$

The reason this is so clever is that energy is conserved using the Verlet algorithm – For other methods (see later) much effort is required to conserve energy.

Verlet algorithm: advance position of each atom and the Kohn-Sham wavefunctions for the electrons in time steps Δt

$$\psi_i^{n+1}(\mathbf{r}) = 2\psi_i^n(\mathbf{r}) - \psi_i^{n-1}(\mathbf{r}) - \frac{(\Delta t)^2}{\mu}\left[\hat{H}\psi_i^n(\mathbf{r}) - \sum_k \Lambda_{ik}\psi_k^n(\mathbf{r},t)\right],$$

$$\mathbf{R}_I^{n+1} = 2\mathbf{R}_I^{n+1} - \mathbf{R}_I^{n-1} + \frac{(\Delta t)^2}{M_I}\mathbf{F}_I. \quad (18.10)$$

Evolves nuclei and electrons conserving energy --- if the constraint of orthonormalization is applied in a "holonomic" (energy conserving) manner – SHAKE algorithm

Problems with Car-Parrinello Unified Algorithm

Basic problems:

1. **Must adjust carefully the fictitious mass" to make calculation efficient and avoid errors**
2. **If states change occupation, this gives extraordinary changes in the fictitious KE – energy transfer to the fictitious degrees of freedom – can be a very large problem in metals**

3. **Allows solutions, but requires expertise!**

What are the key ideas from Car and Parrinello? The steps that lead to very general iterative methods

- optimization methods (instead of variational equations),
- equations of motion (instead of matrix diagonalization),
- fast Fourier transforms (FFTs) – (instead of matrix operations), and
- a trace of occupied subspace (instead of eigenvector operations).

1. **The entire Kohn-Sham problem is a way to find the ground state n(r) and Energy -- Can be solved by minimization methods!**
2. **The variables in the Kohn-Sham approach are the wavefuntions -ψ_i Iterative minimization methods for the wavefunctions instead of diagonalization**
3. **The K-S hamiltonian H is really the gradient of the energy with respect to the wavefunctions – plays the role of a" force" in the iterations The central step is always the operation H ψ_i FFTs make this operation very efficient (All other steps apply with any basis (LCAO, APW, . . .).This step applies only to plane waves -- the key reason why plane waves are so efficient!)**
4. **Need only sum over the occupied states – do not need individual eignevectors!**

Alternatives to Car-Parrinello Unified Algorithm

Basic idea: Use the iterative methods (pioneered by Car and Parrinello) in the "usual approach"

1. **Solve electronic equations by iterative methods**
2. **Calculate forces on atoms**
3. **Move atoms**
4. **Recalculate electrons using the previous density and wavefunctions to generate good starting trial vectors**
5. **Go to step 1 - continue in MD steps**

With advances over the years, can be roughly as efficient as the original Car-Parrinello unified method

Great advantage – straightforward – easy to understand -no major problem for metals – can have efficeint methods the find occupied eigenstates or others that do not.

Can be used with all methods – tight-binding, LCAO, . . .

Iterative Algorithms in Planes Waves I

How do we update the wavefunctions in an iteration?

We always consider the wavefunctions expanded in a basis

$$\psi_i = c_{ij}\,\phi_j$$

and we evolve the values of the coefficients c_{ij} which The energy is a function of the coefficients. These can be considered as variables in a space with dimension (number of occupied states) x (number of basis states)

The equations have exactly the same form for any orthonormal basis and we choose plane waves as the best example. For simplicity of notation we consider Bloch states only at the center of the Brillouin zone, $\mathbf{k} = 0$, in which case the Bloch functions can be written

$$u_i(\mathbf{r}) = \sum_{\mathbf{G}} c_i(\mathbf{G}) \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{G}\cdot\mathbf{r}), \qquad (18.12)$$

where Ω is the volume of the unit cell. Since each band holds one electron per cell (of a given spin) the $c_i(\mathbf{G})$ are orthonormal

$$\sum_{\mathbf{G}} c_i^*(\mathbf{G}) c_j(\mathbf{G}) = \delta_{ij}. \qquad (18.13)$$

Iterative Algorithms in Planes Waves II

How do we update the wavefunctions in an iteration? Continued

The discrete time step equation corresponding to (18.10) becomes

$$c_i^{n+1}(\mathbf{G}) = 2c_i^n(\mathbf{G}) - c_i^{n-1}(\mathbf{G}) - \alpha \left[\sum_{\mathbf{G}'} H(\mathbf{G},\mathbf{G}')c_i^n(\mathbf{G}') - \sum_k \Lambda_{ik} c_k^n(\mathbf{G}) \right], \quad (18.14)$$

A constant α corresponds to Steepest Descent
Improved algorithms include Conjugate Gradient, etc.
(This is the time step term in the CP algorithm)

Lagrange multiplier for orthonormalization
(There are` other approaches – see text)

ALL iterative methods involve the operation of H on the functions ψ which can be done as a matrix multiply

Iterative Algorithms in Planes Waves III

How to carry out the calculations efficiently?

The discrete time step equation corresponding to (18.10) becomes

$$c_i^{n+1}(\mathbf{G}) = 2c_i^n(\mathbf{G}) - c_i^{n-1}(\mathbf{G}) - \alpha \left[\sum_{\mathbf{G}'} H(\mathbf{G},\mathbf{G}')c_i^n(\mathbf{G}') - \sum_k \Lambda_{ik} c_k^n(\mathbf{G}) \right], \quad (18.14)$$

Do not actually do a matrix multiplication! – Kinetic energy is Diagonal in G space --- FFT to real space – Apply potential which is diagonal in real space – inverse FFT back to G space

Update density and hamiltonian to solve self-consistency, update coefficients to solve Schrodinger-like equations for the electrons, and move the nuclei all in one unified algorithm

FFTs instead of matrix multiplies

$$H = T + V$$

Work with each point k separately

In plane waves $T\psi_i k,i = \sum_m \frac{1}{2} (k+ G_m)^2 c_{k,i}(G_m)$

and $V\psi_{k,i} = \sum_n V(r_n)^2 c_{k,i}(r_n)$

No matrices! Only scalars (diagonal matrices)

Find coefficients in real space using FFT
- **Apply potential which is diagonal in real space**
- **Inverse FFT back to G space**
- **Add two parts of wavefunction to get the updated wavefunction in G space**

The matrix multiply have been accomplished by two FFTs and two scalar multiplications

MUCH more efficient for large numbers of plane waves!!

.

What is done in actual codes?

ABINIT

"Band-by-Band" CG minimization
- **Update bands one-by-one with each band forced to be orthogonal to all the ones calculated previously**

Density updated at the same time – complete minimization of energy

VASP

Use a Jacobi-type scheme to find the eigenvector with eigenvalue closest to a chosen energy -- with clever schemes to be sure all eigenvectors are found (none are missing)

SIESTA

Localized orbitals - does not use FFTs

Uses algorithm like CP to update wavefunctions

In all cases:

If atoms are moved use the wavefunctions as starting point for the next step

What is the starting point in actual codes?

An example is:

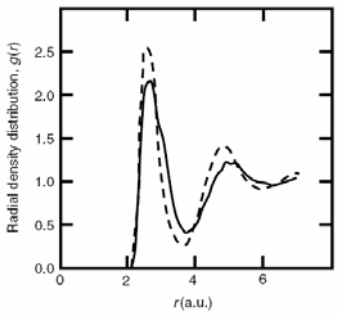
Guess a potential (example -sum of atomic potentials)

Get starting eigenfunctions by diagonalizing a small matrix (needs to be done only once)

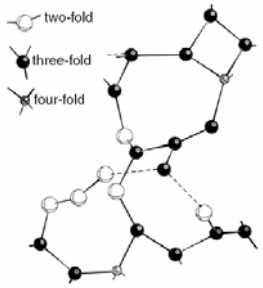
Unified MD – nuclei and electronic states Example of Carbon

Previous ordinary calculations have shown the accuracy of DFT for cabon in crystalline diamond and graphite forms?
The Car-Parrinello method makes it possible to apply the same theory to liquid carbon, high pressure, ... Predictions . . .

Radial density distribution



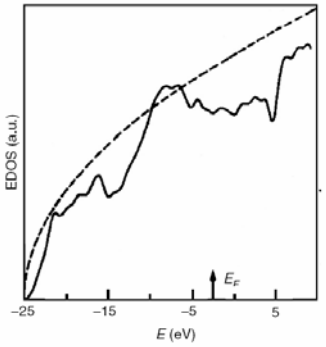
Snapshot



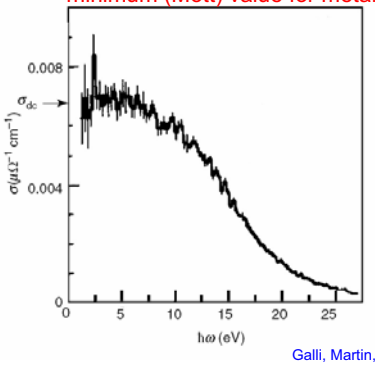
Unified MD – nuclei and electronic states Example of Carbon

Electrical properties --- Is liquid carbon a metal or insulator?

Time averaged density of states – like a metal

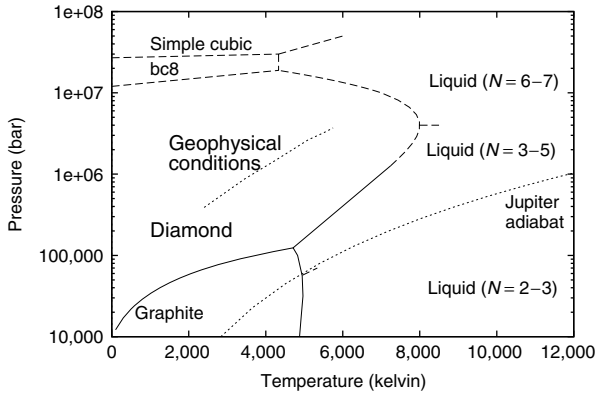


Time averaged electronic canductivity - strong scattering leads to conductivity near the minimum (Mott) value for metals



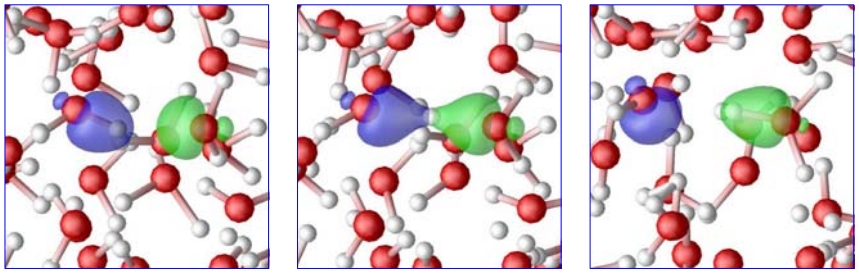
Unified MD – nuclei and electronic states Example of Carbon

Melting of diamond at high pressure – other phases - geophysical, planetary physics



Unified MD using forces – nuclei and electronic states
Water

Simulation of water – many publications – widely-used GGA approximations good – but not good enough – prsent challenge

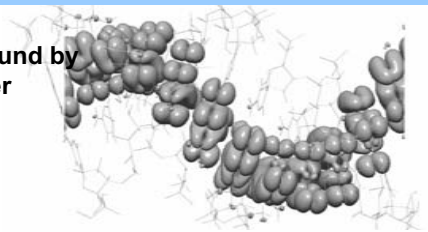


Snapshots of simulation of proton transfer – important process – study of how electrons are transferred as proton moves using localized Wannier functions (later)

Schwegler, Galli

HOMO and LUMO in DNA (SIESTA code)

- Eigenstates found by N^3 method after relaxation
- Could be O(N) for each state



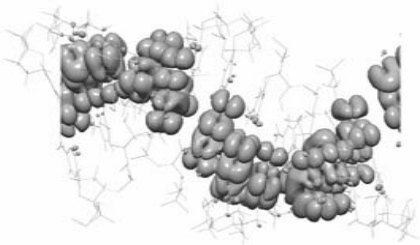
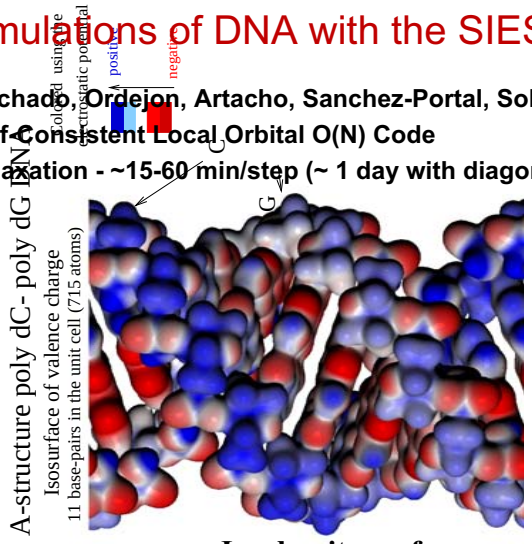


FIG. 1. HOMO bands in symmetric and wagged DNA ($5x10^{-4}$ e/au.^{3})

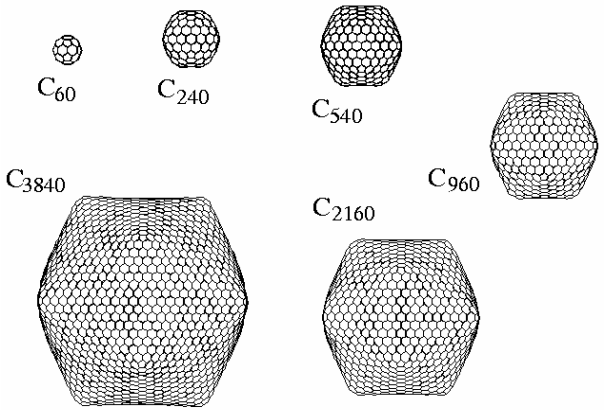
Simulations of DNA with the SIESTA code

- Machado, Ordejon, Artacho, Sanchez-Portal, Soler (preprint)
- Self-Consistent Local Orbital O(N) Code
- Relaxation - ~15-60 min/step (~ 1 day with diagonalization)



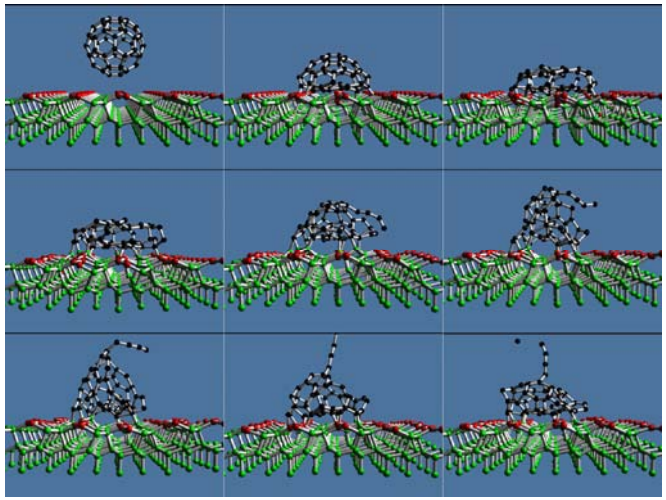
Iso-density surfaces

Example of Relaxation
Prediction of Shapes of Giant Fullerenes using SIESTA



S. Itoh, P. Ordejon, D. A. Drabold and R. M. Martin, Phys Rev B 53, 2132 (1996). See also C. Xu and G. Scuceria, Chem. Phys. Lett. 262, 219 (1996).

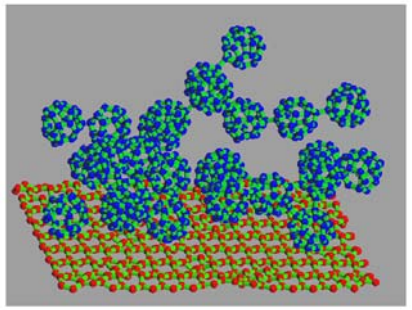
Collision of C_{60} Buckyballs on Diamond Using tight-binding

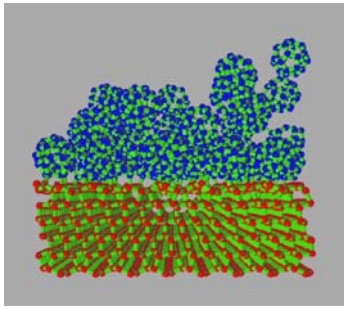


Galli and Mauri, PRL 73, 3471 (1994)

Deposition of C_{28} Buckyballs on Diamond

- **Simulations with ~ 5000 atoms, TB Hamiltonian from Xu, et al. (A. Canning, G.~Galli and J .Kim, Phys.Rev.Lett. 78, 4442 (1997).**





Conclusions

Ideas for minimization and molecular dynamics are from classical mechanic and well-known numerical algorithms
Conjugate gradient, . . .

The Car-Parrinello advance
- **The four ideas that transformed the way calculations are done**
  - **Minimization**
  - **Iteration**
  - **FFTs**
  - **Need only occupied states for n(r) and Energy**

Examples
- **Liquid carbon, Water, . . .**