**UCL** 

# Enhancing Conquest for Accurate, Scalable Simulation of Entire Biological Molecules

Lianheng Tong NAG dCSE Meeting 5th Oct. 2011, Manchester

## Brief Overview of DFT



\* Widely used in Physics, Chemistry, Earth Sciences, Biochemistry

- \* The electronic structure is most important element that determines properties of materials or molecules.
- \* Fundamental physical quantity is the electron density-electronic structure can be written as a functional of the density.
- \* Reworks the many electron problem into noninteracting electrons in an effective potential.
- \* With recent potential functionals can approach "chemical accuracy"

#### Need For Large Scale Calculations For Biomolecules

- \* Complex structures, non-crystalline, require large simulation cells
- \* Presence of multiple possible reaction sites
- \* Geometry of the entire molecule is important
- \* Solvents plays a key role
- \* Spin: Hemes (transition metal ion centre), electron transfer reactions, exact exchange
- \* Van-der-Waals dispersion forces

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## Large Systems: O(N) DFT

- \* Electronic structure is (short) ranged
- For any atom, information depends on the local volume
- \* There is an upper limited on number of interactions on one site
- \* Computer effort should scale linearly
- \* CONQUEST
  - \* FORTRAN 90, MPI
  - \* BLAS, LAPACK, ScaLAPACK, FFT
  - \* Basis: PAOs, B-Splines

#### \* Developers:

- \* UCL: David Bowler, Mike Gillan, Lionel Truflandie, Conn O'Rourke, Umberto Terranova and Lianheng Tong (dCSE)
- \* NIMS, Japan: Tsuyoshi Miyazaki, Michiaki Arita, Takao Otsuka (RIKEN)
- \* NAG: Lianheng Tong (dCSE), CSE support team
- Previous dCSE project: Metal Conquest—Kerker preconditioning, wave-dependent metric, Methfessel-Paxton and k-point parallelisation

\* Works with the one particle density matrix

$$\rho(\mathbf{r},\mathbf{r}') = \sum f_n \psi_n(\mathbf{r}) \psi_n^*(\mathbf{r}')$$

\* We know this decays with distance (Kohn)

 $\rho(\mathbf{r},\mathbf{r}') \to 0, \qquad \|\mathbf{r}-\mathbf{r}'\| \to \infty$ 

\* Locality on the density matrix is achieved by using support functions

 $\phi_{i\alpha}(\mathbf{r}) = \sum b_{i\alpha}{}^{s}\Theta_{s}(\mathbf{r} - \mathbf{R}_{i}), \quad \phi_{i\alpha}(\mathbf{r}) = 0 \text{ if } \|\mathbf{r} - \mathbf{R}_{i}\| > R_{c}$ 



\* Density and Hamiltonian matrix represented by support functions

$$K^{i\alpha j\beta} = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \, \phi^{i\alpha}(\mathbf{r}) \rho(\mathbf{r}, \mathbf{r}') \phi^{j\beta}(\mathbf{r}')$$

$$H^{i\alpha j\beta} = \int d^3 \mathbf{r} \int d^3 \mathbf{r}' \, \phi^{i\alpha}(\mathbf{r}) \hat{H} \phi^{j\beta}(\mathbf{r}')$$

\* Need for idempotency (charge conservation):

$$\mathbf{K}^2 = \mathbf{K}$$

- \* Auxiliary matrix L (McWeeny), fundamental variable  $\mathbf{K} = 3\mathbf{L}^2 2\mathbf{L}^3$
- \* Ground state problem: minimise E with respect to L, subject to the constraint that  $N_e$  is constant.

$$E = \operatorname{tr}(\mathbf{KH}) \quad N_e = \operatorname{tr}(\mathbf{K})$$

- \* Simulation cell divided into spacial partitions
- \* Each partition contain a set of atoms
- Each processor in charge of a set of partitions and all interactions with atoms in the partition



### Million Atoms DFT

- Bulk Si (for covinience)
- \* 512 atoms per core (memory limited)
- \* Cubic cell—cubic number of cores
- Four support functions, slightly coarse grid
- \* Self-consistency done for smaller cells



### Million Atoms PFT

Atoms	Time/core (s)	Energy (Ha)	Cores
4,096	7068.878	-308.268	8
32,768	6893.759	-2,466.150	64
262,144	6931.418	-19,729.202	512
2,097,152	7032.496	-157,833.618	4096

#### Machine: HECToR phase 2a

### **DMPC-gA in Water**



CI

Dimyristoyl-sn-glycerophosphocholine

Phospholipid that incorporates choline as head group.

Important part of cell membrane

Hydrophilic heads in outer surfaces of the bilayer, hydrophobic in between.

\* gramicidin A ion channel allows selective ions (monovalency cations) to pass through cell membrane

 Over 15000 atoms, full DFT (SCF) calculation

Michiaki Arita and Tsuyoshi Miyazaki, 2011

## **DMPC-gA in Water**

- \* Order N with mixed SCF with PCC
- \* SIESTA Pseudo-Potential
- \* Basis: Optimised SZP from DZP (using diagonalisation, piece-wise)
- \* XC Functional: PBE(+D2)
- \* Cores: 512, NIMS Simulator 1
  - \* Intel Xeon processor Nehalem-EP (2.8 GHz), 4 cores/node, 2.85GB per core
- \* SCF computation time: > a week for standard Pulay SCF, < 24 Hrs using mixed SCF (see later)

#### **PMPC-gA in Water**



Michiaki Arita and Tsuyoshi Miyazaki, 2011

### **Adding Spin Polarisation**

\* Consider overall matrices as direct sum of spin components

$$= \begin{pmatrix} \mathbf{L}^{\uparrow} & \mathbf{0} \\ \mathbf{0} & \mathbf{L}^{\downarrow} \end{pmatrix} \equiv \mathbf{L}^{\uparrow} \oplus \mathbf{L}^{\downarrow} \qquad \mathbf{K} = \begin{pmatrix} \mathbf{K}^{\uparrow} & \mathbf{0} \\ \mathbf{0} & \mathbf{K}^{\downarrow} \end{pmatrix} \equiv \mathbf{K}^{\uparrow} \oplus \mathbf{K}^{\downarrow} \qquad \mathbf{H} = \begin{pmatrix} \mathbf{H}^{\uparrow} & \mathbf{0} \\ \mathbf{0} & \mathbf{H}^{\downarrow} \end{pmatrix} \equiv \mathbf{H}^{\uparrow} \oplus \mathbf{H}^{\downarrow}$$

\* Properties of direct sum  $(A \oplus B)(C \oplus D) = (AC) \oplus (BD)$   $(A \oplus B) + (C \oplus D) = (A + C) \oplus (B + D)$  $tr(A \oplus B) = tr(A) + tr(B)$ 

#### \* The spin dependence in H only comes from exchange-correlation

$$\mathbf{H}^{\sigma} = \mathbf{T} + \mathbf{V}_{\text{local}} + \mathbf{V}_{\text{H}} + \mathbf{V}_{\text{NL}} + \mathbf{V}_{\text{xc}}^{\sigma}$$

\* Hence

$$E = \sum_{\sigma} \operatorname{tr}(\mathbf{K}^{\sigma} \mathbf{H}^{\sigma}) \equiv \sum_{\sigma} E^{\sigma} \qquad N = \sum_{\sigma} \operatorname{tr}(\mathbf{K}^{\sigma}) \equiv \sum_{\sigma} N^{\sigma}$$

\* We assume first that support functions are spin independent

 $\Phi_{i\alpha}(\mathbf{r}) = \phi_{i\alpha}^{\uparrow}(\mathbf{r}) \oplus \phi_{i\alpha}^{\downarrow}(\mathbf{r})$ 

 $\phi_{i\alpha}^{\uparrow}(\mathbf{r}) = \phi_{i\alpha}^{\downarrow}(\mathbf{r}) = \phi_{i\alpha}(\mathbf{r})$ 

L

### **Energy Minimisation**

- \* Minimise E with respect to  $\mathbf{L}^{\uparrow}$  and  $\mathbf{L}^{\downarrow}$
- L<sup>↑</sup> and L<sup>↓</sup> are fundamental variables and hence assumed to be independent from each other
- \* Subject to constraints
  - \* Total number of electrons fixed, OR
  - Number of electrons in each spin channel is fixed —constant magnetisation
- \* Band energy is only dependent explicitly on  $\mathbf{L}^{\sigma}$ through  $E^{\sigma} = \operatorname{tr}(\mathbf{K}^{\sigma}\mathbf{H}^{\sigma})$
- \* Hamiltonian of one spin channel is independent of  $\mathbf{L}^{\sigma}$  of the other channel

### **Energy Minimisation**

- \* Use Pulay minimisation scheme:
  - \* Start from a list histories  $\mathbf{L}_1^{\sigma}, \dots, \mathbf{L}_n^{\sigma}$
  - \* Find search direction  $G_n$  from  $L_n$
  - \* We work on the direct sum, treating it as one vector, not on the individual spin components
  - \* Take a step along  $G_n$  and then find the optimised  $L_n$  using n

$$\bar{\mathbf{L}}_{n+1} = \alpha_{n+1}\mathbf{L}_{n+1} + \sum \alpha_i \bar{\mathbf{L}}_n$$

\* Minimisation problem = find  $\alpha_i$  so that  $\bar{\mathbf{G}}_{n+1}$  is minimum, subject to the constraint  $\sum_{i=1}^{n+1} \alpha_i = 1$ 

i

\* Correct  $\mathbf{L}_n$  to give the same electron number

## Finding Search Direction

- \* Search direction is defined as
  - Fixed total electron number only (spin populations are allowed to change)

$$\mathbf{G}^{\sigma} = -\frac{\partial E}{\partial \mathbf{L}^{\sigma}} + \sum_{\sigma} \frac{\partial E}{\partial \mathbf{L}^{\sigma}} \cdot \frac{\partial N_{e}}{\partial \mathbf{L}^{\sigma}} \frac{\partial N_{e}}{\partial \mathbf{L}^{\sigma}} \frac{\partial N_{e}}{\partial \mathbf{L}^{\sigma}} \frac{\partial N_{e}}{\partial \mathbf{L}^{\sigma}} \frac{\partial N_{e}}{\partial \mathbf{L}^{\sigma}}$$

\* Fixed spin population and total electron number

$\mathbf{C}^{\sigma}$ –	$\partial E$	$\frac{\partial E}{\partial \mathbf{L}^{\sigma}} \cdot \frac{\partial N_e}{\partial \mathbf{L}^{\sigma}} \partial N_e$
<b>G</b> –	$-\partial \mathbf{L}^{\sigma}$ $+$	$\frac{\partial N_e}{\partial \mathbf{L}^{\sigma}} \cdot \frac{\partial N_e}{\partial \mathbf{L}^{\sigma}} \partial \mathbf{L}^{\sigma}$
		$OL^{\circ} OL^{\circ}$

 The definition of search direction is the only difference between the two electron number constraints



## Spin Pulay Mixing (Self-Consistency)

#### \* Standard Pulay mixing scheme

$$R_i = R(\rho_i^{\text{opt}}) = \sum_j^i \alpha_j (\rho_j^{\text{out}} - \rho_j^{\text{in}})$$



\* Solving Lagrange multiplier problem gives

$$\alpha_i = \frac{\sum_j A_{ij}^{-1}}{\sum_{ij} A_{ij}^{-1}}, \quad A_{ij} = \int \mathrm{d}^3 \mathbf{r} \, R_i(\mathbf{r}) R_j(\mathbf{r})$$

\* Spin polarisation: 2n degrees of freedom, needs 2n equations:  $\alpha_i$  must be spin dependent  $\alpha_i^\sigma$ 



### Spin Pulay Mixing (Self-Consistency)



### **Mixed E-Minimisation and SCF**



- \* One realise at self-consistent ground state,  $\frac{\partial E}{\partial \mathbf{L}^{\sigma}}$  is also zero.
- May combine the Pulay process of minmisation with SCF
- \* Pulay coefficients  $\alpha_i$  need not dependent on spin because L is a direct sum of its components

### **Mixed E-Minimisation and SCF**



#### **Mixed E-Minimisation and SCF**



### **Conclusion and Future Work**

- \* Conquest already scales efficiently
- \* Implementation of Spin Polarisation 95% finished
- Introduced new standard pulay mixing procedure for spin polarised calculations
- Mixed SCF dramatically improves stability and convergence. However its efficiency on spin polarised systems is still to be tested
- Current Van-der-Waals forces are implemented using empirical D2 (NIMS)
- Will soon implementing parallelised version of Langreth-Lundqvist functional for ab initio Vander-Waals.

# Thank you for your attention!