

# Solving the DFT equations: exact vs iterative diagonalization

Matt Probert

*August-Wilhelm Scheer Visiting Prof TUM 2015*

Condensed Matter Dynamics Group

Department of Physics,

University of York, U.K.

<http://www-users.york.ac.uk/~mijp1>

- The Kohn-Sham equations
- Naïve approach – exact diagonalization
- Smart approach – iterative solver
  - Car-Parrinello vs Conjugate Gradients
- Summary

# The Kohn-Sham equations

- Rewrite the many-body Schrödinger equation for  $N$  electrons into  $N$  1-particle equations:

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + V[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r}) \right\} \psi_b(\mathbf{r}) = \epsilon_b \psi_b(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_{j=1}^N |\psi_j(\mathbf{r})|^2$$

- And occupy each band  $b$  with 2 electrons
- This looks like a set of eigenvalue equations ...



- How can we represent a wavefunction in a computer?
  - Real-space grid will require very dense mesh to get required resolution
  - Alternatively could write it in terms of coefficients of known basis functions ...
- Obvious basis set for periodic system is 3D sine and cosine functions -> Fourier series and so can combine with Bloch's theorem:

- 3D Fourier basis (also known as *plane waves*):

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{G}\mathbf{k}} e^{i(\mathbf{G}+\mathbf{k})\cdot\mathbf{r}}$$

- where  $c_{\mathbf{G}\mathbf{k}}$  are unknown complex coefficients
- The sum is over all wavevectors  $\mathbf{G}$  which fit the unit cell and  $\mathbf{k}$  comes from Bloch's theorem
- Hence  $\psi_{\mathbf{k}}$  is a vector of coefficients  $c_{\mathbf{G}\mathbf{k}}$
- And can truncate sum at a finite  $\mathbf{G}_{\max}$  as

$$|\mathbf{G}| \rightarrow \infty, |c_{\mathbf{G}\mathbf{k}}| \rightarrow 0$$

- The K-S equations can be written in simple form using the Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V[\rho](\mathbf{r})$$

- Hence the set of K-S equations can be rewritten as an eigenvalue problem:

$$H[\rho]\psi_{bk} = \epsilon_{bk}\psi_{bk}$$

- Where the Hamiltonian  $H[\rho]$  is an Hermitian matrix of size  $N_G \times N_G$  and  $\psi_{bk}$  is a vector of  $N_G$  Fourier coefficients

# Exact Diagonalization

- So we want to solve

$$\mathbf{H}[\rho]\psi_{bk} = \epsilon_{bk}\psi_{bk}$$

- to find the eigenenergies  $\epsilon_{bk}$  and  $\psi_{bk}(\mathbf{r})$  eigenfunctions which we represent in terms of the coefficients  $c_{Gk}$
- For a simple matrix problem  $\mathbf{H}\mathbf{x}=\lambda\mathbf{x}$  we can solve by *diagonalizing*  $\mathbf{H}$ 
  - BUT unlike simple problems we do not know the matrix elements of  $\mathbf{H}$  before we start!

- Note that H depends on V
  - And V is a functional  $V[\rho]$
  - And  $\rho$  depends on  $\psi$
  - And we are trying to diagonalize H to find  $\psi$ !
  
- Hence we must solve iteratively:
  - Guess an initial  $\psi \rightarrow \rho \rightarrow V[\rho] \rightarrow H$
  - Solve  $H\psi = \epsilon\psi$  to get new approximate  $\psi$
  - Repeat to convergence ...

- Given the above, we can make an  $N_G \times N_G$  matrix  $H$  and diagonalize it
  - Standard linear algebra packages can do this in  $O(N_G^3)$  operations and  $O(N_G^2)$  storage
  - And must repeat for each k-point  $\mathbf{k}$
  - And iterate to self-consistency
- How big is  $N_G$ ?
  - Consider a  $10\text{\AA}^3$  box and cut-off energy of 500 eV then  $N_G \sim 50600$
  - Estimate time  $\sim 12$  hrs/iteration at 3 GFLOPs

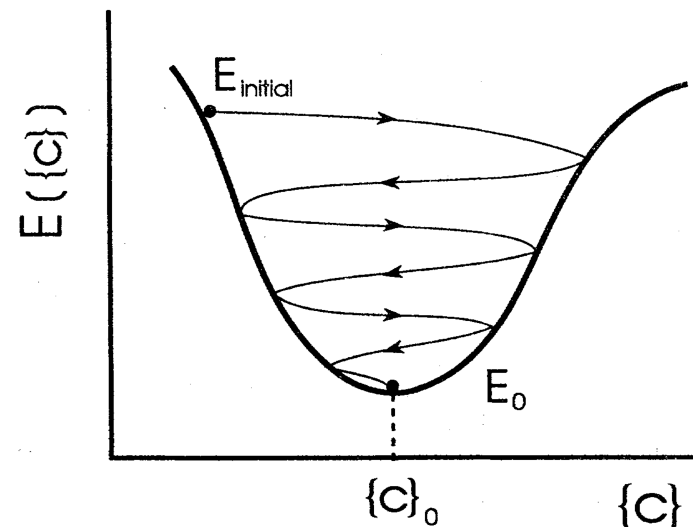
- 
- Exact diagonalization is VERY expensive
    - And an  $N_G \times N_G$  matrix has  $N_G$  eigenvalues
    - But typically only want the lowest few eigenvalues  $\sim N_{electrons}$
    - And takes a lot of computer power to get machine precision in all eigenvalues which have to do for every iteration even when far from self-consistency
  - State of the art up until 1985
    - Limited DFT to a max of  $\sim 10$  electrons!



# **Iterative Diagonalization - indirect approach**

- Car and Parrinello (1985)
  - Inspired by extended Lagrangian methods in Molecular Dynamics
  - Introduced fictitious 'mass' and 'kinetic energy' for each  $c_{Gk}$

Do MD with damping in the space of  $c_{Gk}$  so as system 'cools' it converges to ground state value of  $c_{Gk}$  and hence electron density etc.



- Major algorithmic break through!
- Cost  $\sim O(N_G^2 N_b)$  to apply H to all bands
  - And explicit orthogonalization step costs  $\sim O(N_G N_b^2)$
  - BUT  $N_b \ll N_G \dots$
  - And once got to ground state can combine with conventional MD of ions to get *ab initio* MD for the first time
- Still requires  $\sim O(N_G^2)$  storage

- But to ensure adiabatic separation of electrons and ions need mass separation
  - Choose very small ‘mass’ for  $c_{Gk}$
- Hence need very small time step to integrate the equations of motion
  - Hence not actually that much faster than exact diagonalization in ‘time to science’
  - And cannot handle metals due to adiabatic issues

- One view of the C-P approach was that it could be seen as indirect energy minimization
  - But simulated annealing is VERY inefficient – better for global than local optimization
- So why not use a more efficient direct function minimization approach?
  - Conjugate-gradients introduced by Teter, Payne & Allan (1989) along with an efficient pre-conditioner
  - Objective: energy eigenvalues

# **Iterative Diagonalization - direct approach**

- The groundstate energy  $E_0$  is the lowest possible energy of the system
- Any wavefunction has energy  $E \geq E_0$  so
  - Guess a trial wavefunction  $\psi$
  - Compute  $E = \psi^\dagger H \psi$
  - Tweak  $c_G$  to lower  $E$
  - When we cannot lower  $E$  any more then  $\psi$  is the groundstate!
  - Variational principle in action

- Efficient minimization methods need both objective function and its derivative
- Functional calculus time:

$$\begin{aligned}\epsilon_{bk} &= \frac{\psi_{bk}^\dagger \mathbf{H} \psi_{bk}}{\psi_{bk}^\dagger \psi_{bk}} \\ \Rightarrow \frac{\delta \epsilon_{bk}}{\delta \psi_{bk}^\dagger} &= \frac{\left(\psi_{bk}^\dagger \psi_{bk}\right) \mathbf{H} \psi_{bk} - \left(\psi_{bk}^\dagger \mathbf{H} \psi_{bk}\right) \psi_{bk}}{\left(\psi_{bk}^\dagger \psi_{bk}\right)^2} \\ &= \mathbf{H} \psi_{bk} - \epsilon_{bk} \psi_{bk}\end{aligned}$$

- And so gradient vanishes at minimum ...



- Start with  $\psi_j$  and compute  $\epsilon_j$
- Compute the gradient  $\frac{\delta \epsilon_j}{\delta \psi_j^\dagger}$ 
  - This is the change to  $c_G$  that increases  $\epsilon_j$
  - We want to decrease  $\epsilon_j$  so use negative
- Guess new eigenstate  $\psi_j^{new} = \psi_j - \lambda \frac{\delta \epsilon_j}{\delta \psi_j^\dagger}$
- Vary  $\lambda$  until found min  $\epsilon_j$  in this direction
  - This is called the *line minimization* step
- Update, recompute gradient, repeat ...

- If apply this procedure then will quickly find lowest eigenstate  $\psi_1$
- Repeating it for  $\psi_2$  will give same answer!
- The solution is to explicitly orthogonalize so

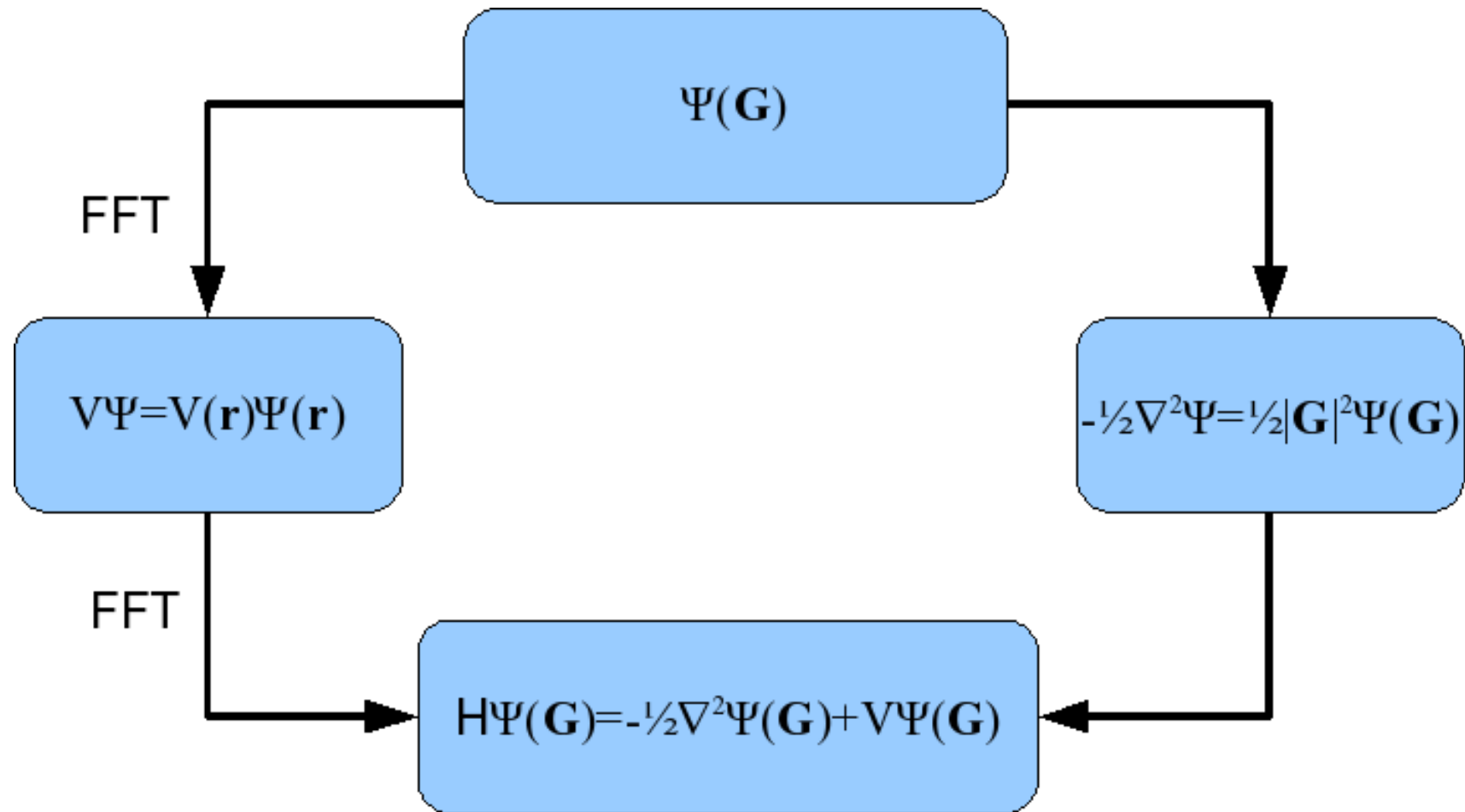
$$\psi_2^\dagger \psi_1 = 0$$

- So need good matrix algebra package/code for multiplication, orthogonalization ....

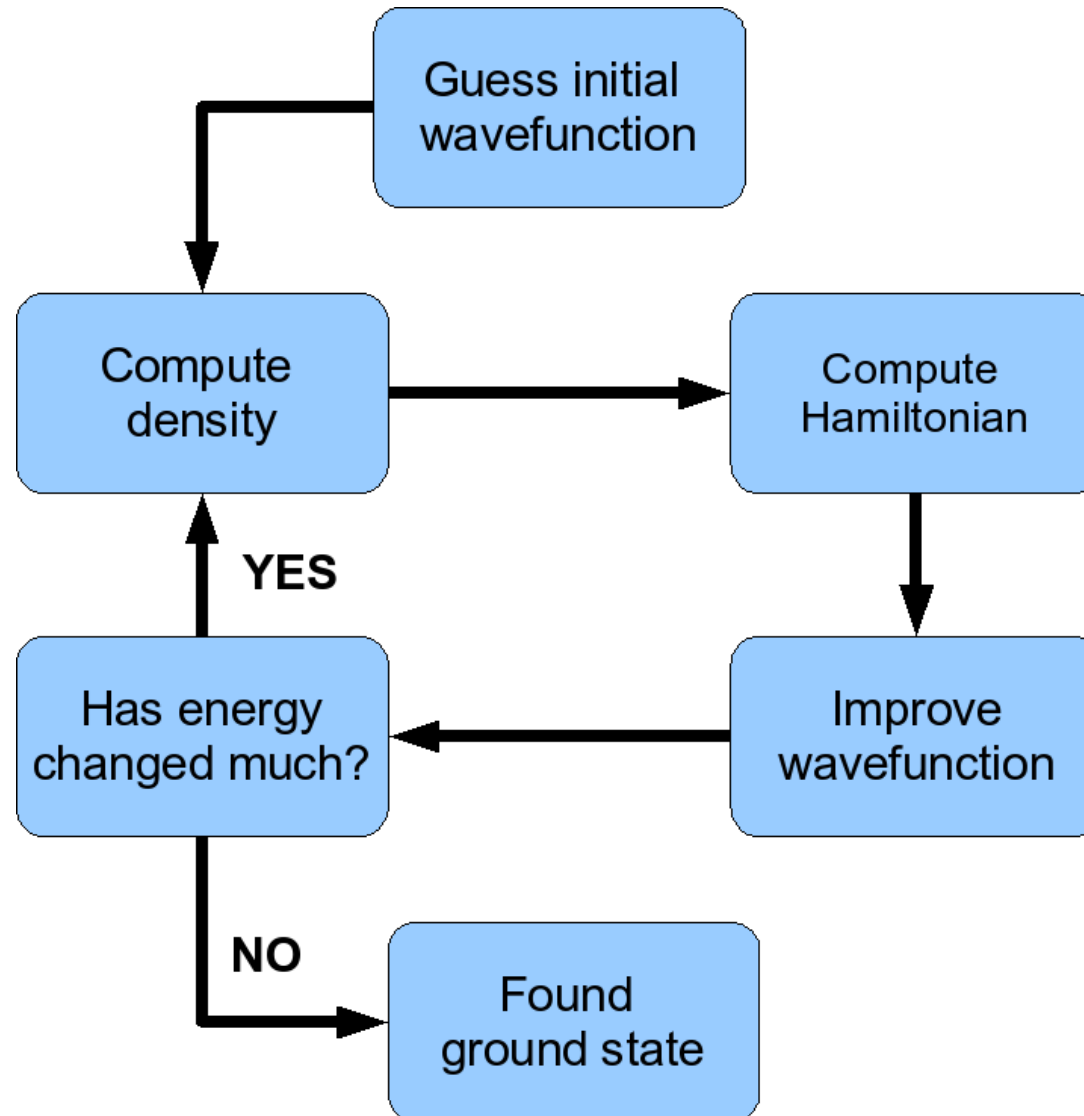
- Remember:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V[\rho](\mathbf{r})$$

- So can split into two terms:
- Kinetic energy – trivial to apply in reciprocal space:  $\nabla^2\psi_{bk}(\mathbf{G}) = -|\mathbf{G} + \mathbf{k}|^2\psi_{bk}(\mathbf{G})$
- Potential energy – trivial to apply in real space:  $V[\rho](\mathbf{r})\psi_{bk}(\mathbf{r})$
- Hence use Fast Fourier Transforms to switch spaces ...



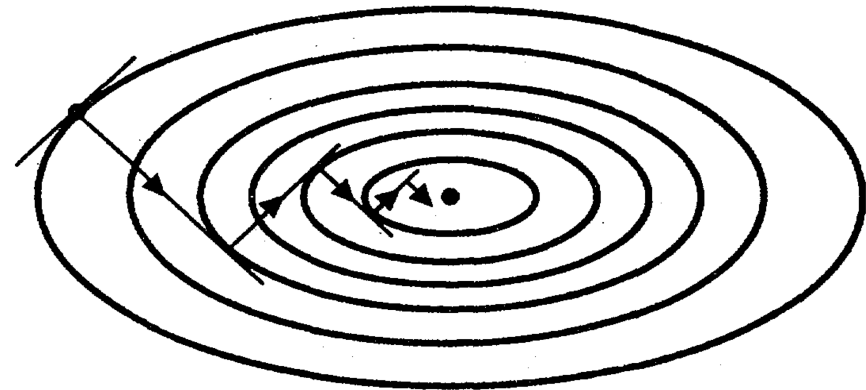
# Finding the Groundstate



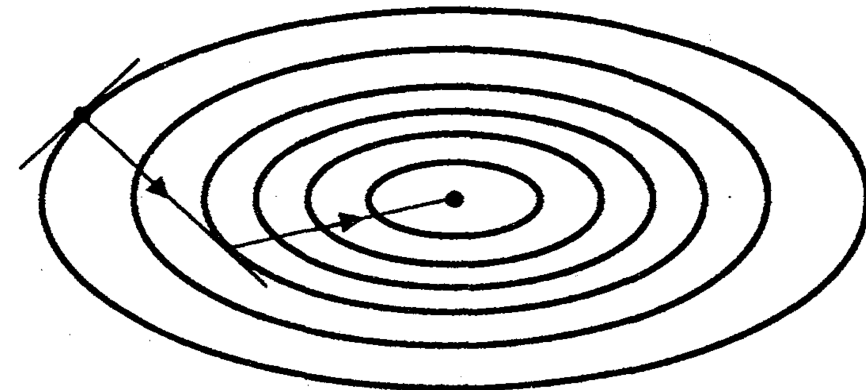
- Steepest descents works – robust but slow
- Conjugate gradients is more efficient
- Both schemes have similar advantages:
  - Never need to store H explicitly
    - Hence storage  $\sim O(N_G)$
  - Smart use of real/reciprocal space means cost of applying H  $\sim O(N_G N_B)$
  - Orthogonalization of bands  $\sim O(N_B^3)$
  - Cost of FFT  $\sim O(N_G N_B \ln N_G)$

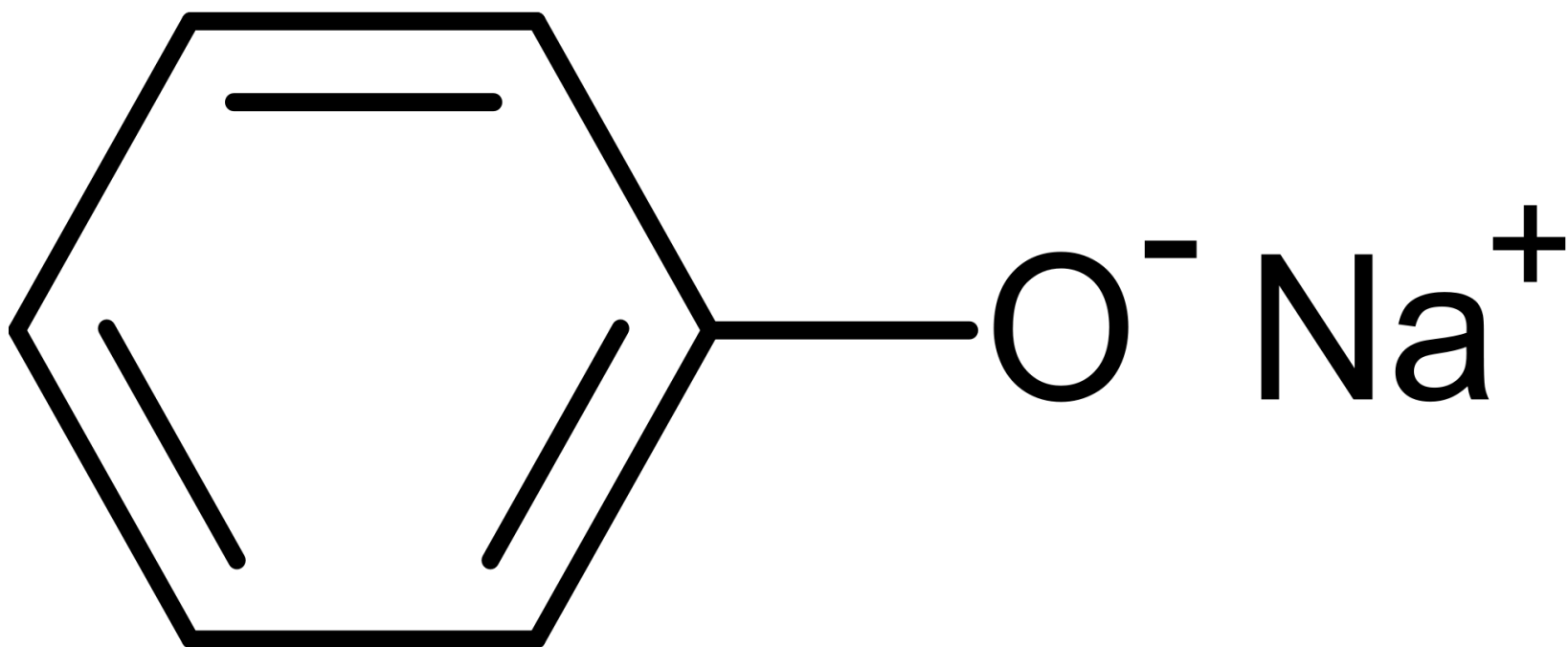
- More details on SD and CG tomorrow ...
- CG makes better choice of search direction
- Pre-conditioned CG better still
- CASTEP uses p-CG and more recent advances ...

STEEPEST DESCENTS



CONJUGATE GRADIENT









- Direct minimization does not need adiabatic separation of electrons and ions
  - Hence handles metallic states easily
- Once got ground state can use Hellman-Feynman theorem to get forces and hence do Born-Oppenheimer MD
  - With a much bigger time step than C-P
  - Traditionally had worse energy conservation than C-P but no longer true with recent developments such as XL-BOMD

# Summary

- DFT reduces QM to a matrix eigenvalue problem
  - Where number of useful eigenstates is SMALL compared to size of matrix
  - Hence iterative diagonalization is best
  - No need to converge each band robustly until near to ground state
- Need efficient implementations of matrix multiplication, orthogonalization and FFTs

- MC Payne et al., Rev. Mod. Phys **64**, 1045 (1992)
- WH Press et al, “*Numerical Recipes: The Art of Scientific Computing*”, Cambridge University Press (1989 - 2007)
- RM Martin, “*Electronic Structure: basic theory and practical methods*”, Cambridge University Press (2004)
- SJ Clark, MD Segall, CJ Pickard, PJ Hasnip, MIJ Probert, K Refson and MC Payne, “*First principles methods using CASTEP*”, Zeitschrift für Kristallographie **220**, 567 (2005)