

Concepts and Math Problems in Electronic Structure Calculations

Lin-Wang Wang

Scientific Computing Group

- **Many-body Schrodinger's equations**
- **Density functional theory and single particle equation**
- **Selfconsistent calculation/nonlinear equation/optimization**
- **Optical properties**
- **Basis functions for wavefunctions**
- **Pseudopotentials**
- **Technical points in planewave calculations**

Many body Schrodinger's equation



Schrodinger's equation (1930's): the great result of reductionism !

$$\left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N, t) = i \frac{\partial}{\partial t} \Psi(r_1, \dots, r_N, t)$$

All the material science and chemistry is included in this equation !

The challenge: to solve this equation for complex real systems.

For stationary solution: $\Psi(r_1, \dots, r_N, t) = e^{-i\omega t} \Psi(r_1, \dots, r_N)$

$$\left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N) = E \Psi(r_1, \dots, r_N)$$

The famous Einstein formula: $E = \hbar\omega$

Ground state: the lowest E state; Excited state: higher E state.

Electrons are elementary particles, two electrons are indistinguishable

$$\Psi(r_1, \dots, r_i \dots r_j \dots r_N) = \alpha \Psi(r_1, \dots, r_j \dots r_i \dots r_N)$$

$$\alpha^2 = 1$$

$\alpha = 1$, **Boson: phonon, photon, W-boson, Higgs-boson,**

(usually particles which transmit forces)

$\alpha = -1$, **Fermion: electron, proton, neutron, quark, muon,**

(usually particles which constitute the matter)

For our case: electron

$$\Psi(r_1, \dots, r_i \dots r_j \dots r_N) = -\Psi(r_1, \dots, r_j \dots r_i \dots r_N)$$

Many body wavefunctions

$$\Psi(r_1, \dots, r_i \dots r_j \dots r_N) = -\Psi(r_1, \dots, r_j \dots r_i \dots r_N) \quad \text{antisymmetric}$$

$$\iiint |\Psi(r_1, \dots, r_N)|^2 dr_1 \dots dr_N = N \quad \text{normalized}$$

One example of the antisymmetric wavefunction: Slater determinate

$$\Psi(r_1 \dots r_N) = \begin{vmatrix} \Phi_1(r_1) & \dots & \Phi_N(r_1) \\ \dots & \dots & \dots \\ \Phi_1(r_N) & \dots & \Phi_N(r_N) \end{vmatrix}$$

This is the exact solution for:

$$\left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N) = E \Psi(r_1, \dots, r_N)$$

The partial differential equation becomes separable

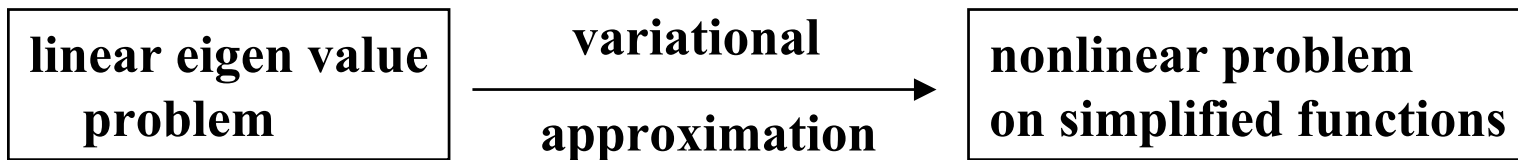
Another way to look at it: variational methods



$$E = \iiint \Psi(r_1, \dots, r_N) \left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$

The ground state corresponds to the optimized state Ψ which is antisymmetric and normalized.

So, we can try variational Ψ for whatever expressions we like



Plug in the Slater determinate for Ψ , we have (Hartree-Fock equation):

$$\left\{ -\frac{1}{2} \nabla^2 + \sum_R \frac{Z}{|r - R|} + \int \frac{\rho(r')}{|r - r'|} dr' \right\} \varphi_i(r) + \sum_j \int \frac{\varphi_j(r)}{|r - r'|} \varphi_j(r') \varphi_i(r') dr' = E_i \varphi_i(r)$$

Some concepts and terminologies



$$\Psi(r_1 \dots r_N) = \begin{vmatrix} \Phi_1(r_1) & \dots & \Phi_N(r_1) \\ \dots & \dots & \dots \\ \Phi_1(r_N) & \dots & \Phi_N(r_N) \end{vmatrix}$$

E_i

- $\Phi_j(\mathbf{r})$: single particle orbital
- One orbital can only have one electron (2 include spin)
----- Pauli exclusion principle
- $\Phi_1, \Phi_2, \dots, \Phi_N$ the N occupied single particle orbitals
- We also have: $\Phi_{N+1}, \Phi_{N+2}, \dots$ the unoccupied orbitals
- Using one of $\Phi_{N+1}, \Phi_{N+2}, \dots$ to replace one of $\Phi_1, \Phi_2, \dots, \Phi_N$
the resulting Slater determinant will correspond to one excited state
- For the lowest excited state: $E_{excited} - E_{ground} \approx E_{N+1} - E_N$ (band gap)

Energy breakup

$$E_{tot}^{HF} = \sum_i -\frac{1}{2} \int \varphi_i(r) \nabla^2 \varphi_i(r) dr + \int \sum_R \frac{Z}{|r - R|} \rho(r) dr + \frac{1}{2} \int \frac{\rho(r') \rho(r)}{|r - r'|} dr' dr$$

kinetic

Electron-ion

Electron Coulomb

$$+ \sum_{i,j} \int \frac{\varphi_j(r) \varphi_i(r) \varphi_j(r') \varphi_i(r')}{|r - r'|} dr' dr$$

Exchange energy

$$E_{\text{corr}} = E_{\text{exact}} - E^{HF}$$

Whatever left from HF

Kinetic: ~ 40 eV/atom Coulomb: ~ 40 eV/atom

Exchange: ~ 20 eV/atom Correlation: ~ 4 eV/atom

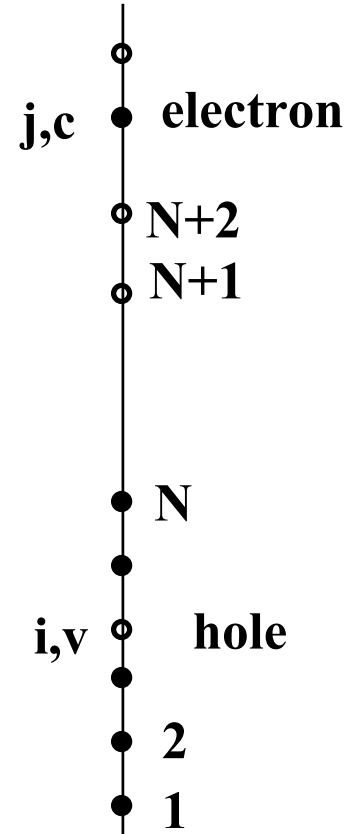
Typical chemical bond: ~ 2 eV

For chemical accuracy, we need: ~ 0.05 eV/atom

Every term is important

Different configurations: CI

$$SD_{conf}(r_1, \dots, r_N) = \begin{vmatrix} \Phi_1(r_1) & \dots & \Phi_{j,c}(r_1) & \dots & \Phi_N(r_1) \\ \dots & \dots & \dots & \dots & \dots \\ \Phi_1(r_N) & \dots & \Phi_{j,c}(r_N) & \dots & \Phi_N(r_N) \end{vmatrix}$$



CI: configuration interaction

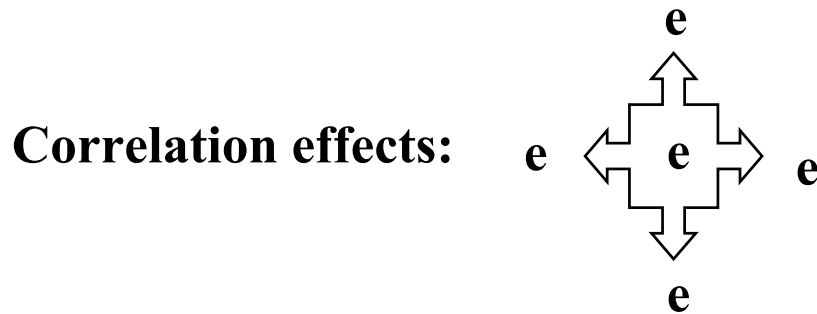
$$\Psi(r_1, \dots, r_N) = \sum_{config} C(config) SD_{config}(r_1, \dots, r_N)$$

The number of configuration is exponential, only feasible for a few atom systems.

Judicious selection of configurations: → MP2, coupled-cluster, etc

Traditional quantum chemistry approaches

More on variational many-body wavefunctions



One electron at r will repulse other electrons near r due to Coulomb inter.

$$\Psi(r_1 \dots r_N) = \exp\left[-\sum_i \chi(r_i) - \sum_{ij} u(|r_i - r_j|)\right] \begin{vmatrix} \Phi_1(r_1) & \dots & \Phi_N(r_1) \\ \dots & \dots & \dots \\ \Phi_1(r_N) & \dots & \Phi_N(r_N) \end{vmatrix}$$

Jastrow factor

Unfortunately, cannot break down the following integration.

$$E = \iiint \Psi(r_1, \dots, r_N) \left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$

Using Monte-Carlo method to do the integration: variational quantum MC.

Diffusion quantum Monte-Carlo approach



$$\left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N, t) = i \frac{\partial}{\partial t} \Psi(r_1, \dots, r_N, t)$$

This looks like a classical diffusion equation with finite temperature

$$\left\{ D \nabla^2 + V(\vec{r}) - \mu \right\} S(\vec{r}, t) = \frac{\partial}{\partial t} S(\vec{r}, t) \quad S(\mathbf{r}, t) \rightarrow \text{particle density}$$

Using classical Monte-Carlo to simulate the random movements of particles in a 3N dimension space.

Problem: S is always positive, but ψ has both positive and negative due to antisymmetry \rightarrow **the famous sign problem !**

Fix nodal approx: use	$\Phi_1(\mathbf{r}_1) \dots \dots \Phi_N(\mathbf{r}_1)$ $\Phi_1(\mathbf{r}_N) \dots \dots \Phi_N(\mathbf{r}_N)$	to divide the 3N space into positive and negative compartments, move articles within.
-----------------------	---	---

Another approach: the density matrix method



$$E = \iiint \Psi(r_1, \dots, r_N) \left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_{i,R} \frac{Z}{|r_i - R|} \right\} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$

$$E = \iiint \delta(r_1 - r_1') \delta(r_2 - r_2') \left\{ -\nabla_1^2 + \frac{1}{|r_1 - r_2|} + \sum_R \frac{Z}{|r_1 - R|} \right\} \rho(r_1, r_1'; r_2, r_2') dr_1 dr_1' dr_2 dr_2'$$

$$\rho(r_1, r_1'; r_2, r_2') = \iint \Psi(r_1, r_2, r_3, \dots, r_N) \Psi(r_1', r_2', r_3, \dots, r_N) dr_3 \dots dr_N$$

Great, reduce the N variable function into a 4 variable function !!

Problem: $\rho(r_1, r_1'; r_2, r_2')$ might not be N-representable !

- Many necessary conditions to make ρ N-representable
- The ρ is within some hyperdimension convex cone.
- Linear programming optimization approach
- Recent work: Z. Zhao, et.al, it can be very accurate, but it is still very expensive (a few atoms).
- No known sufficient condition

The density functional theory



$$\rho(r_1) = \iint \Psi(r_1, r_2, r_3, \dots, r_N) \Psi(r_1, r_2, r_3, \dots, r_N) dr_2 \dots dr_N$$

Any single particle $\rho(r)$ is N-representable.

Can we use ρ as one basic variable to determine all other things ?

$$E = \iiint \Psi(r_1, \dots, r_N) \left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_i V(r_i) \right\} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$

$V(r)$ is one basic variable which determines everything.

So $V \rightarrow \rho$, Now, can $\rho \rightarrow V$? (ρ uniquely determine V)

We need to prove: we cannot have $V_1 \rightarrow \rho$, and $V_2 \rightarrow \rho$.

Density functional theory (continued)



$$E = \iiint \Psi(r_1, \dots, r_N) \left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_i V(r_i) \right\} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$

We need to prove: we cannot have $V_1 \rightarrow \rho$, and $V_2 \rightarrow \rho$.

Suppose this happens, then $V_1 \rightarrow \Psi_1 \rightarrow \rho$ and $V_2 \rightarrow \Psi_2 \rightarrow \rho$

- Since Ψ_1 is the variational minimum of V_1 , so: $E(V_1, \Psi_1) < E(V_1, \Psi_2)$

$$E_K[\Psi_1] + E_{Coul}[\Psi_1] + \int V_1(r) \rho(r) dr < E_K[\Psi_2] + E_{Coul}[\Psi_2] + \int V_1(r) \rho(r) dr$$

$$E_K[\Psi_1] + E_{Coul}[\Psi_1] < E_K[\Psi_2] + E_{Coul}[\Psi_2] \quad \text{Eq(1)}$$

- Since Ψ_2 is the variational minimum of V_2 , so: $E(V_2, \Psi_2) < E(V_2, \Psi_1)$

$$E_K[\Psi_2] + E_{Coul}[\Psi_2] < E_K[\Psi_1] + E_{Coul}[\Psi_1] \quad \text{Eq(2)}$$

Eq(1),(2) contradict with each other, so we cannot have $V_1 \rightarrow \rho$, and $V_2 \rightarrow \rho$

We can also prove, smooth ρ is V -representable (i.e, can find a $V \rightarrow \rho$)

In summary, V is a functional of ρ , thus everything is a functional of ρ

$\Psi[\rho]$ exists, so:

$$E = \iiint \Psi(r_1, \dots, r_N) \left\{ -\sum_i \frac{1}{2} \nabla_i^2 + \sum_{i,j} \frac{1}{|r_i - r_j|} + \sum_i V(r_i) \right\} \Psi(r_1, \dots, r_N) dr_1 \dots dr_N$$



$$E[\rho] = E_{kin}[\rho] + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + E_{xc}[\rho] + \int V(r)\rho(r) dr$$

Great, change the problem to a fluid-dynamics like problem, just one func. $\rho(r)$

Problem: DFT proves that $E_{kin}[\rho]$, $E_{xc}[\rho]$ exist, but they are unknown.

Many approx. for $E_{kin}[\rho]$: Thomas-Fermi, Gradient Expan., Wang-Teter.

L. Sham's idea: approximate $E_{kin}[\rho]$ by $\int -\frac{1}{2} \sum_i \varphi_i(r) \nabla^2 \varphi_i(r) dr$

and $\rho(r) = \sum_i |\varphi_i(r)|^2$, $\{\varphi_i(r)\}$ are orthonormal.

Use local density approximation (LDA) for $E_{xc}[\rho]$:

$$E_{xc}[\rho] = \int \varepsilon_{xc}(\rho(r)) dr$$

Find function $\varepsilon_{xc}(\rho)$ from simple systems: homogeneous electron gas, where
The total energy has been calculated by QMC. **The Perdew-Zunger paper.**

Now, we have the LDA formula:

$$E_{LDA} = -\frac{1}{2} \sum_i \int \varphi_i(r) \nabla^2 \varphi_i(r) dr + \frac{1}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + \int \varepsilon_{xc}(\rho(r)) dr + \int V(r)\rho(r) dr$$

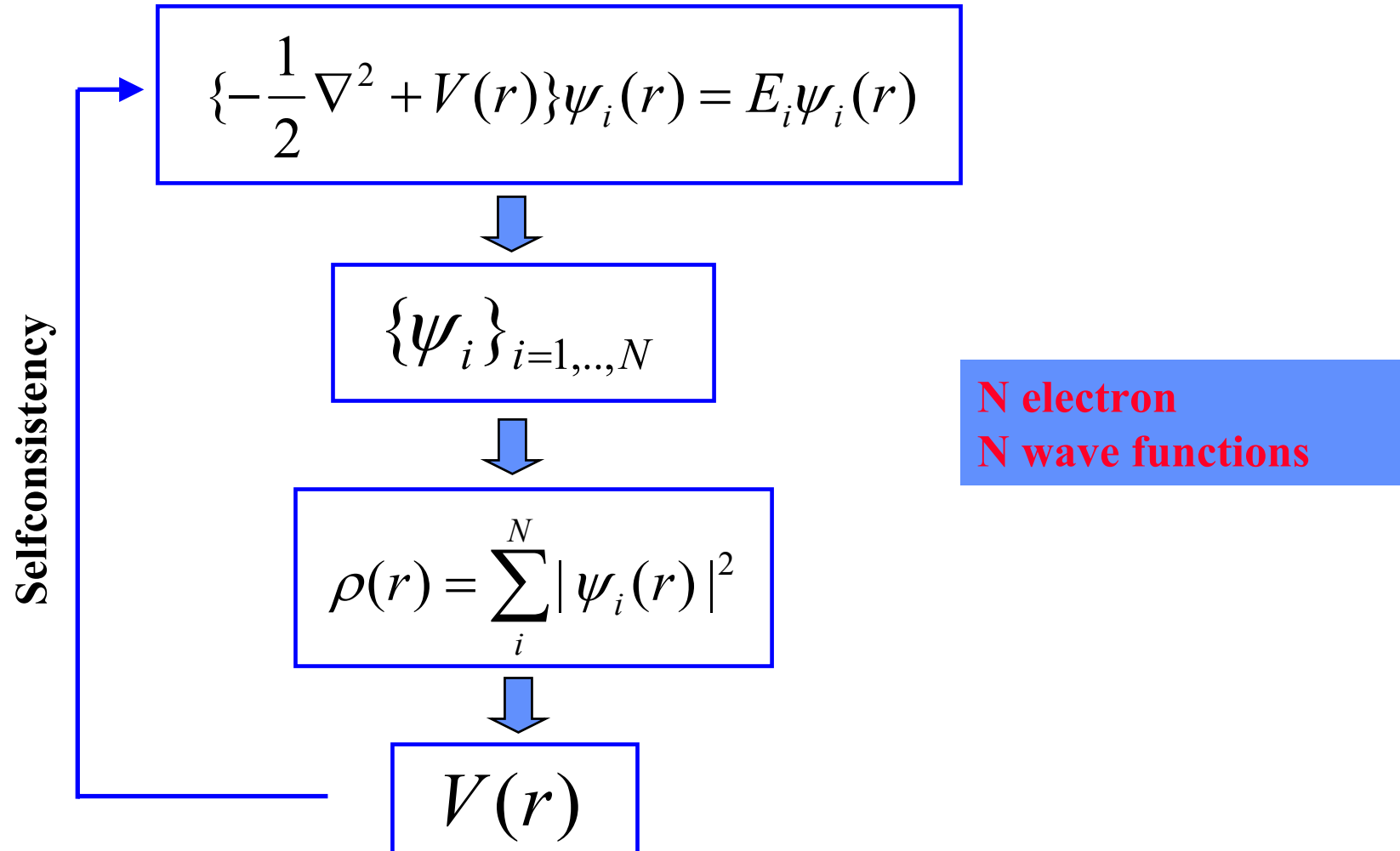
The ground state solution is a minimum of E_{LDA} for variational $\{\varphi_i(\mathbf{r})\}$

The variational minimum condition: (Kohn-Sham equation)

$$\left\{ -\frac{1}{2} \nabla^2 + V_{LDA}(r) \right\} \varphi_i(r) = E_i \varphi_i(r)$$

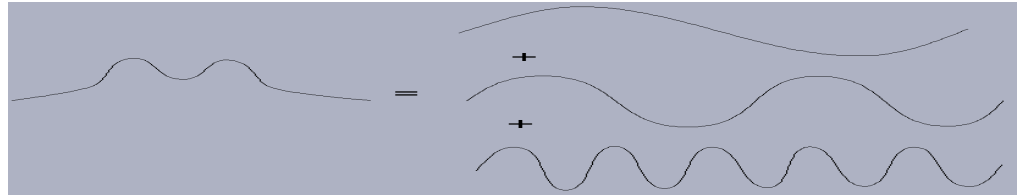
and:
$$V_{LDA}(r) = \int \frac{\rho(r')}{|r-r'|} dr' + \mu_{xc}(\rho(r)) + V(r)$$

Selfconsistent calculations



Planewave expansion of the wavefunction

$$\psi(r) = \sum_q C(q) e^{iqr}$$



Diagonal representation

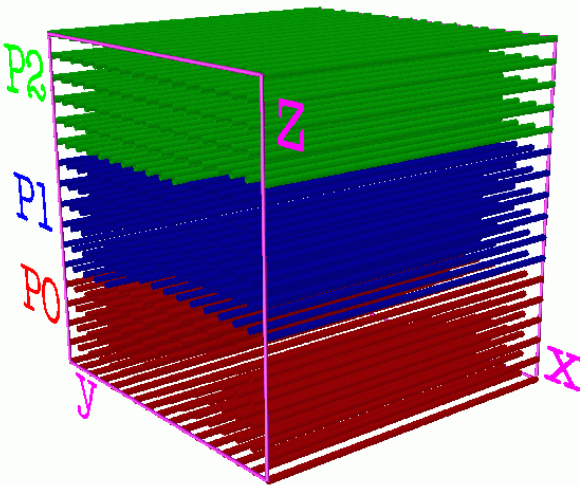
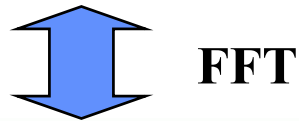
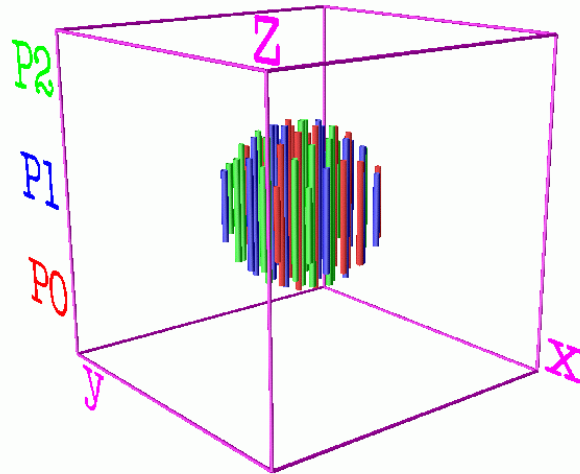
$$\left\{ -\frac{1}{2} \nabla^2 + V(r) \right\} \psi_i(r) = E_i \psi_i(r)$$

diagonal
in q space

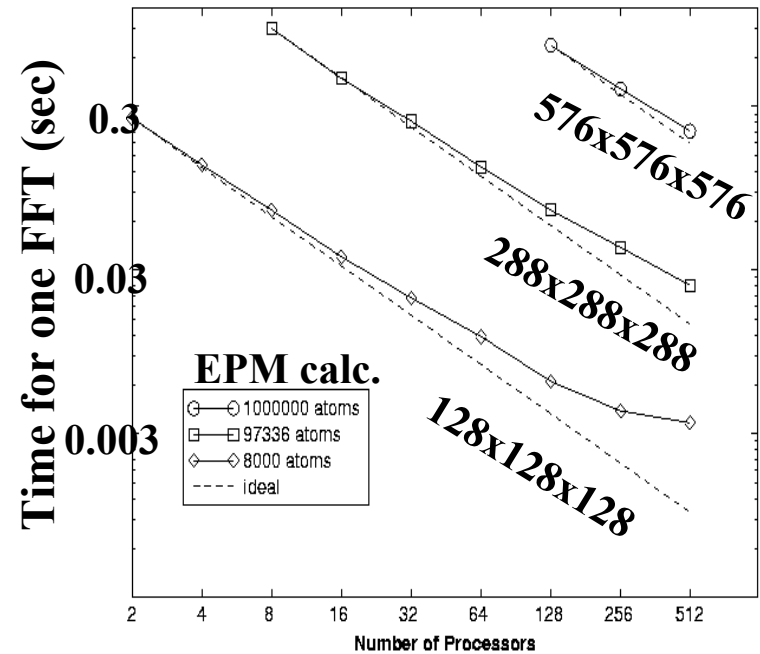
diagonal
in real space

Fast Fourier Transformation between
real space $\psi(r)$ and Fourier space $C(q)$.

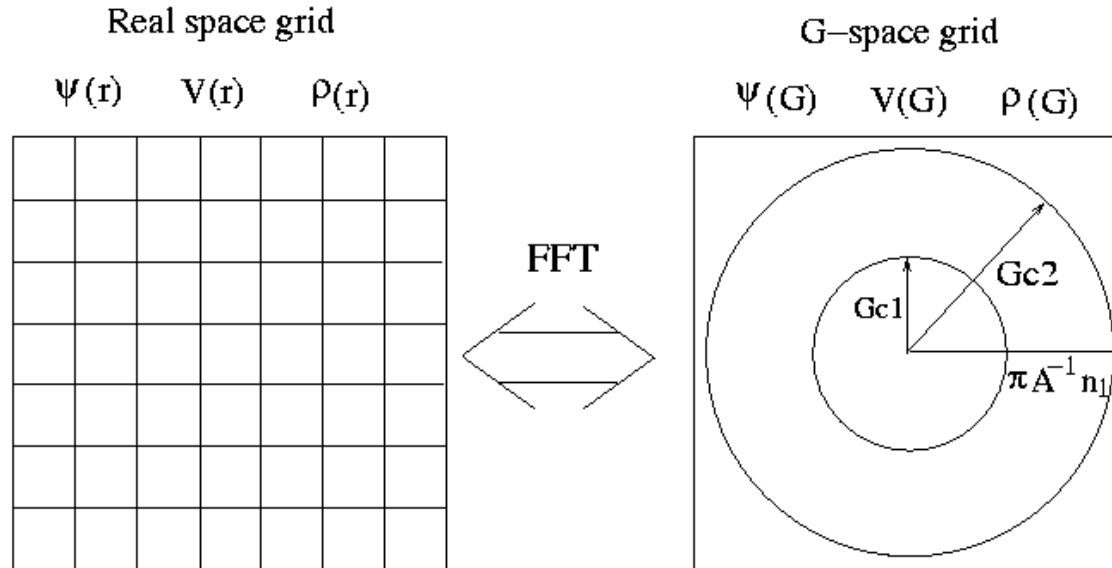
A parallel Fast Fourier Transformation code



- Specially designed for PW elec. structure calculation.
- Work load balance
- Memory balance
- Minimum communication



FFT grids



$G_{c1} < 0.5 G_{c2}$, so:
$$\int V(r) \psi^2(r) dr = \Delta \Omega \sum_{grid-i} V'(r_i) \psi^2(r_i)$$

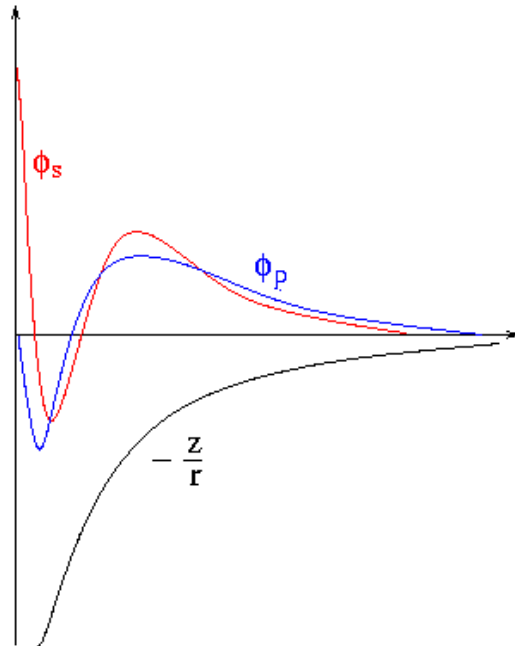
It doesn't have the usual $1/h^2$ discretization error, it is exact!

We are not doing the usual discretization

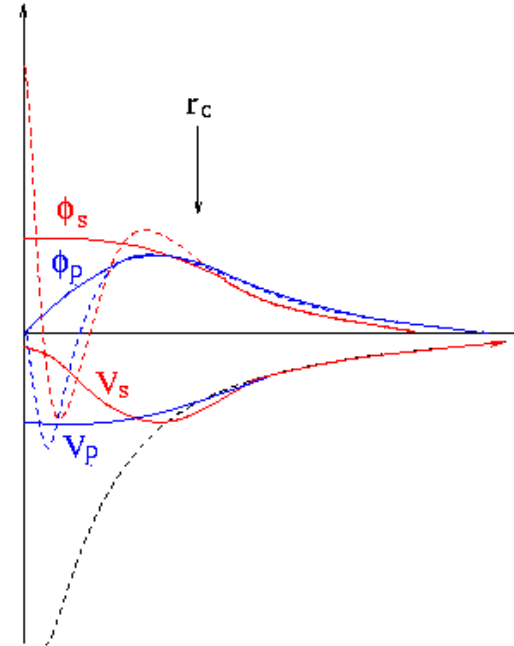
Note: $V'(r_i) \neq V(r_i)$:
$$V(r) = \int_0^{\infty} e^{iqr} V(q) dq \quad , \quad V'(r) = \int_0^{Gc2} e^{iqr} V(q) dq$$

Pseudopotentials

Original wavefunctions
and potential



The pseudo-wavefunctions
and potentials



The price: need additional nonlocal potential.

KB form:
$$\widehat{V}_{nonloc} \varphi(r) = \sum_{R,ref} W_{R,ref}(r) \int W_{R,ref}(r') \varphi(r') dr'$$

A few types of eigen value problems



- (1) Total energy calculations: need all the occupied states (5% of the all lowest eigenstates). Need them inside a outer loop**

- (2) Nonselfconsistent optical property calculations: need a few states at the interior of the spectrum. One shot calculation.**

- (3) Transport problems: a special eigenstate problem, need eigenstates under special boundary conditions.**

Total energy problem



$$\left\{-\frac{1}{2}\nabla^2 + V(r)\right\}\psi_i(r) = E_i\psi_i(r) \quad \text{Need: } \{\psi_i\}_{i=1,\dots,N}$$

(1) The explicit matrix H is only available for very small systems (used in 70's).

(2) For large systems, $H\psi$ is done using FFT (due space representation), so iterative methods are used.

(3) Current methods:

CG on Grassman's manifold:

$$\text{Min} \langle \psi_i | H | \psi_i \rangle$$

Under constraint:

$$\langle \psi_i | \psi_j \rangle = \delta_{ij}$$

(4) Band by band algorithm vs all band algorithm

Total energy problem (continue)

(1) Davison's method vs CG method

(2) Residual minimization method / direct inversion in the iterative subspace (RMM-DIIS)

Using $\phi_l = HR_{l-1}$ to generate a Krylov subspace $\{\phi_l\}$
and use $\{\phi_l\}$ to get the minimum residual

$$R_l = (H - \langle \psi_l | H | \psi_l \rangle) \psi_l$$

This by itself is very slow, but subspace diagonalization
saves the algorithm

Doing each band independently, avoid orthogonalization

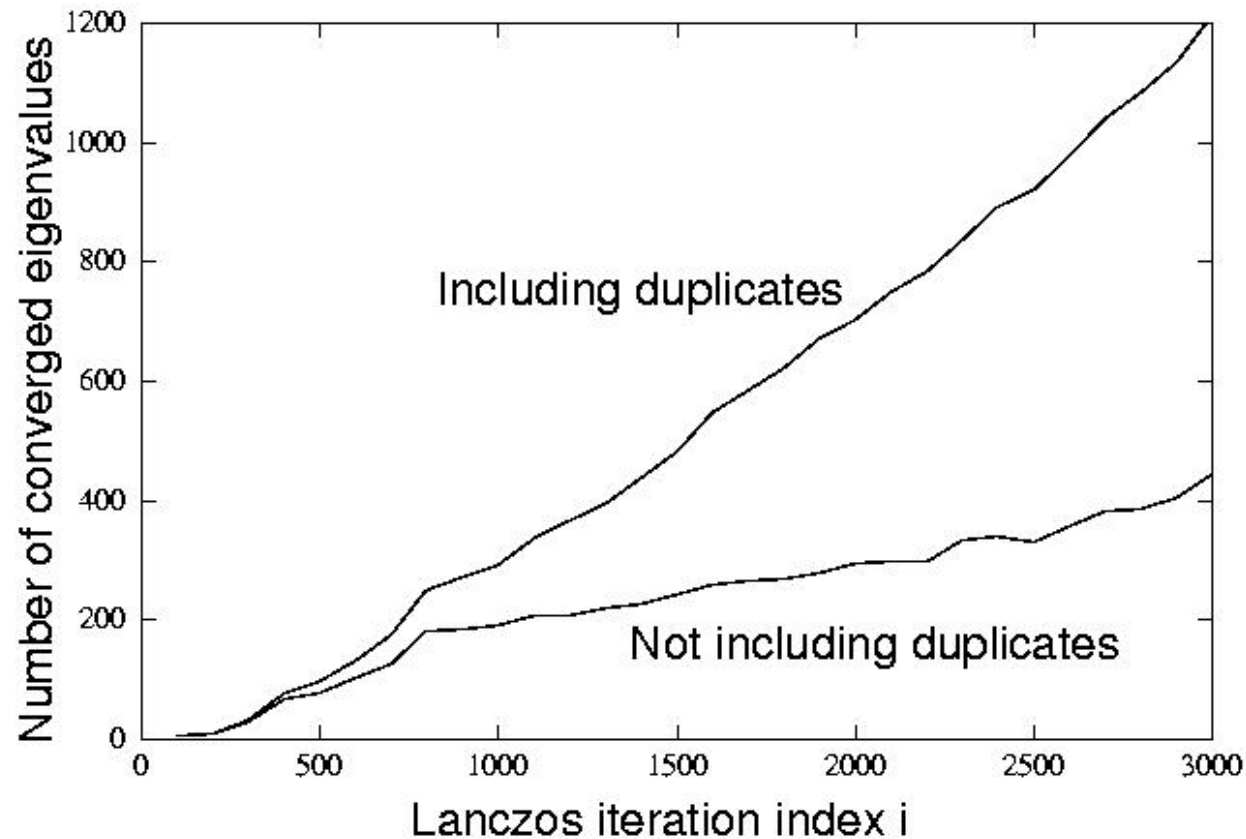
Total energy problem (continue)



(1) Preconditioning: kinetic energy, diagonal precondition

(2) Lanczos method: can be very fast.

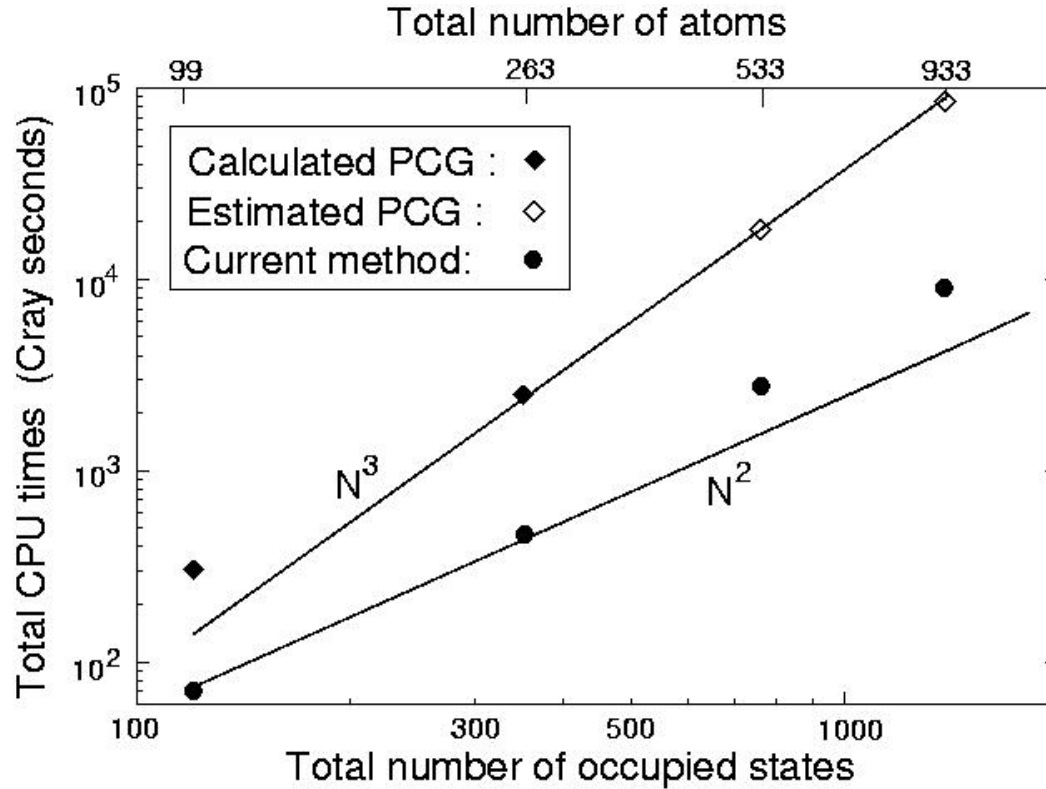
Long Lanczos iteration (10,000) without explicit orth.



Total energy calculation (continue)



Lanczos is faster than CG even without preconditioning.

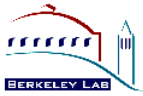


Challenge: (1) how to use preconditioning. (2) how to restart.

Wish list for total energy calculation algorithms

- (1) Iterative method based on $H\psi$**
- (2) Preconditioning, if possible.**
- (3) Restart from previously converged states.**
- (4) Share Krylov space vectors among eigenstates (Lanczos type methods).**
- (5) Avoid frequent orthogonalization among the eigenstates.**

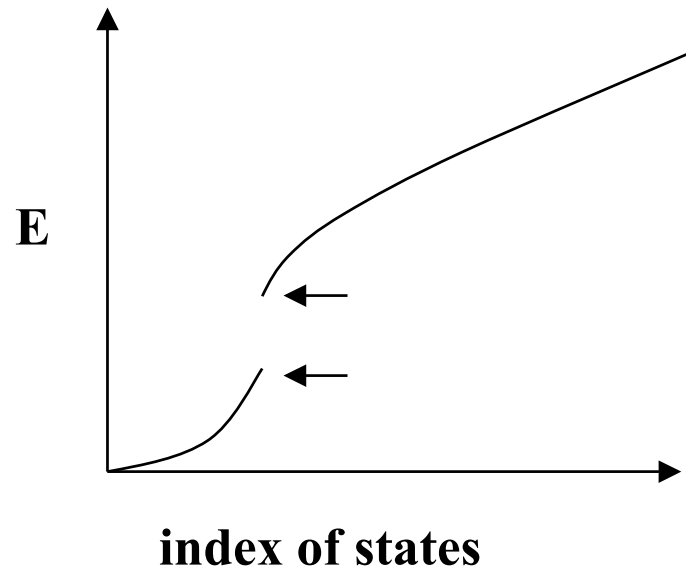
Interior eigenstate problem



The challenge: H is not explicitly known, cannot be inverted

Have to rely on iterative methods.

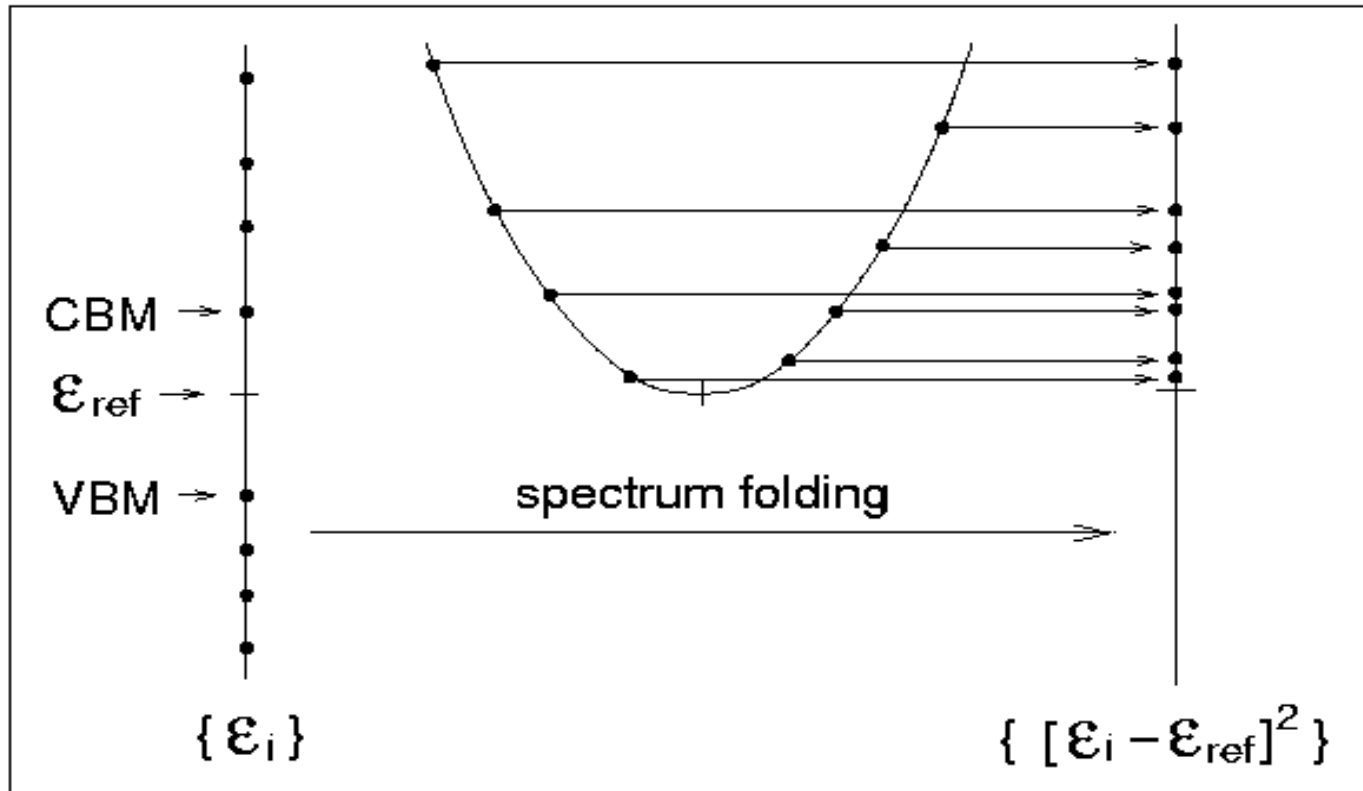
Typically there is a gap in the spectrum, only interested in gap edge states.



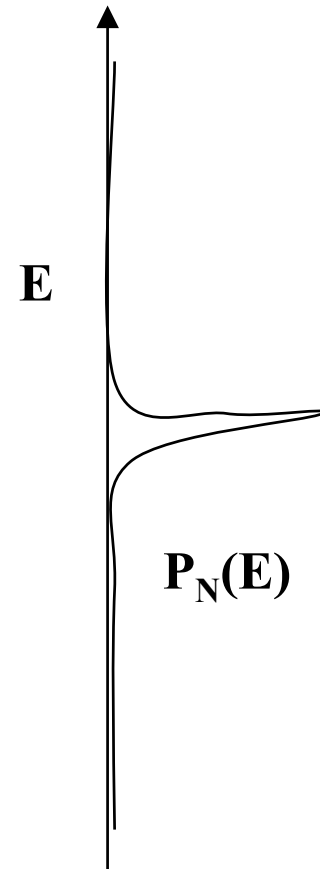
Folded Spectrum Method and Escan Code

$$H\psi_i = \varepsilon_i\psi_i$$

$$(H - \varepsilon_{ref})^2 \psi_i = (\varepsilon_i - \varepsilon_{ref})^2 \psi_i$$



- (1) We can try other methods on $(H-E_{\text{ref}})^2$, e.g, Lanczos
- (2) Outer / inner loop methods: inner loop try to approximately invert $Hy=x$. Does it worth it?
How do they compare to direct, one-loop method?
- (3) Jacobi-Davison method.
- (4) Challenge: current method works on $(H-E_{\text{ref}})^2$, the condition number is much worse than H . Can any interior eigenstate method be as easy as working on H ?
- (5) Is interior eigenstate problem intrinsically hard for iterative methods.
$$\psi_i = P_N(H)\phi_{\text{random}}$$



$$\left\{-\frac{1}{2}\nabla^2 + V(r)\right\}\psi_i(r) = E_i\psi_i(r)$$

**Using 3D 7 points finite difference formula for ∇^2 ,
H is a sparse matrix in real space grid presentation.
The resulting H' can be factorized directly using
 $\sim 200 N_{\text{grid}}$. Then $H'y=x$ can be solved in a linear scaling.**

**This can be used as a preconditioning, or help to solve
the original $Hy=x$.**

**Some problems: there are nonlocal parts in $V(r)$, thus
it is not really diagonal in real space.**

The transport problems

We want to solve:
$$\left\{-\frac{1}{2}\nabla^2 + V(r)\right\}\psi(r) = E\psi(r)$$

for a given E inside a real space domain,
outside this domain (or at the boundary), we have
special boundary conditions, e.g:

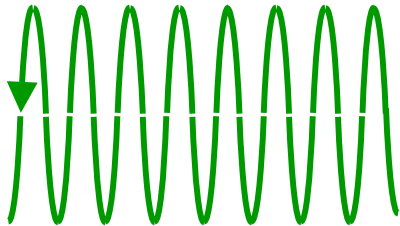
$$\psi(r) = \exp(ik(E) \cdot r) + \beta \exp(-ik(E) \cdot r)$$

$$\psi(r) = \alpha \exp(ik(E) \cdot r)$$

$$\psi(r) = \exp(ik(E) \cdot r)$$

$$+ \beta \exp(-ik(E) \cdot r)$$

$$\psi(r) = \alpha \exp(ik(E) \cdot r)$$



$$\left\{-\frac{1}{2}\nabla^2 + V(r)\right\}\psi(r) = E\psi(r)$$

