# Electronic Structure Calculation

divide the methods generally:

- wavefunction based methods (quantum chemistry methods),
  Hartree-Fock, Configuration Interaction, Møller-Plesset perturbation Theory, etc.
- electronic density methods,
  Density Functional Theory (DFT), Time-Dependent DFT, Tight-binding DFT, etc.
- semi-empirical methods

Used indistinctly by physicists and chemists nowadays, but the former were developed by chemists and the later by physicist.

Goal: Solve the stationary Schrödinger equation: $\hat{H}_{el}\psi = \varepsilon\psi$

where $\psi = \psi(r_1, r_2, \cdots, r_{N_e})$ is the many-electron wavefunction.

Assuming that there is a complete set of single particle spin-orbitals: $\phi_{i,\sigma} \equiv \phi_n$

$\Phi_k(r_1, r_2, \cdots, r_{N_e})$

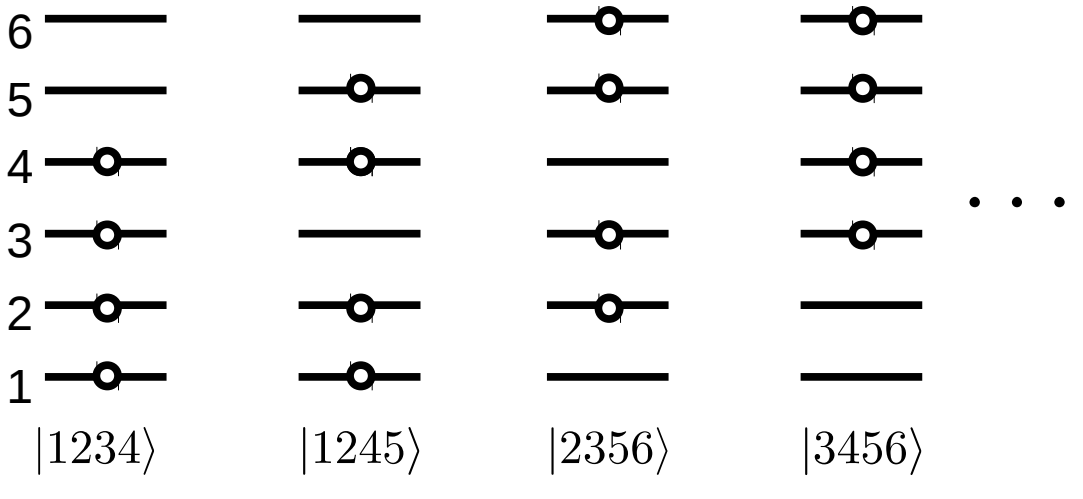
is a possible configuration, with k = ($n_1$,$n_2$, …) for the various spin-orbitals in various ways with $N_e$ electrons, and properly anti-symmetrized.

The Slater determinant representation

$$\Phi_k(r_1, r_2, \cdots, r_{N_e}) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \phi_{n_1}(r_1) & \phi_{n_2}(r_1) & \phi_{n_3}(r_1) & \cdots \\ \phi_{n_1}(r_2) & \phi_{n_2}(r_2) & \phi_{n_3}(r_2) & \cdots \\ \phi_{n_1}(r_3) & \phi_{n_2}(r_3) & \phi_{n_3}(r_3) & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix}.$$

The most general state $\psi(r_1, r_2, \cdots, r_{N_e}) = \sum_k C_k \Phi_k(r_1, r_2, \cdots, r_{N_e})$

sum over all possible configurations $k = |n_1, n_2, \cdots\rangle$



Expanding $\psi$ via determinants, we arrive at the secular equation

$$\sum_{k'} \left(H_{k,k'} - \varepsilon\delta_{k,k'}\right) C_{k'} = 0$$

with eigenstates $|\psi_a\rangle = \sum_k C_{k,a}|\Phi_k\rangle$

The method outlined is called Configuration Interaction (CI).
It relies on a proper choice of

- spin-orbitals
- a finite set of representative configurations

Problem is that the number of configurations quickly increases with the number of spin-orbitals (n)

total number of configurations is $\binom{n}{N} = \dfrac{n!}{(n-N_e)!N_e!}$

Example, for a single $H_2O$ molecule, that has 10 electrons. Using just 10 atomic orbitals, times 2 spin states (20 spin-orbitals), the total configurations is 184756.

# Electronic Structure Calculation: Variational Calculus

In order to find and approximate solution we can use the variational method in which a certain form of the wavefunctions is written in terms of unknown parameters

$$E(\xi) = \langle \psi(\xi) | \hat{H} | \psi(\xi) \rangle \ , \qquad \langle \psi(\xi) | \psi(\xi) \rangle = 1$$

The minimum of $\varepsilon(\xi)$ cannot be lower than the real ground state.

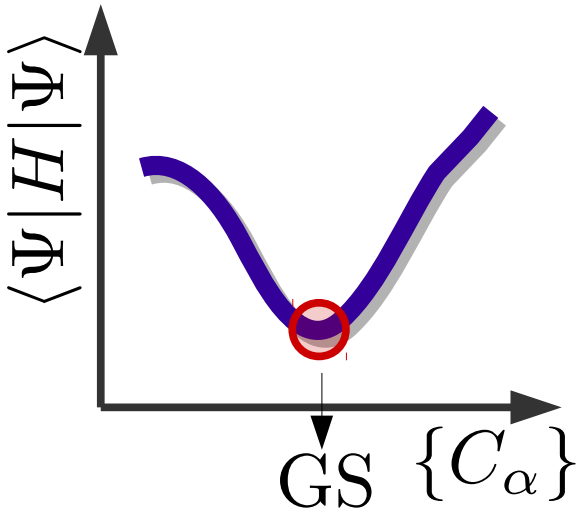
$$\left. \begin{array}{c} \langle \psi(r;\xi) | \hat{H} | \psi(r;\xi) \rangle \\ \\ E\left(\xi\right) : \xi \rightarrow E\left(\xi\right) \end{array} \right\} \Longrightarrow \left\{ \begin{array}{c} \langle \psi | \hat{H} | \psi \rangle \\ \\ E\left[\psi\right] : \psi \rightarrow E\left[\psi\right] \end{array} \right.$$

Variational Principle for the Hartree-Fock Method:

$$\delta E\left[\psi\right] = E\left[\psi + \delta\psi\right] - E\left[\psi\right] = 0$$

In practical situations: $\psi(r) = \sum_a C_a \varphi_a(r)$

the variational parameter: $\delta\psi \equiv \{\delta C_a\} \equiv \delta\xi$



# Hartree-Fock Self Consitent Field (HF-SCF) Method

The simplest wavefunction for a many-body system is given by the Hartree-Fock method, which takes into account only one configuration for the system (just one Slater determinant). Therefore, in this case there is only correlation due to particle exchange.

In any case, the configuration must be an eigenstate of the total spin.
Assuming that the hamiltonian does not contain spin operators.

$$\begin{aligned} \hat{S}^2 &\longrightarrow \hbar^2 S(S+1) \\ \hat{S}_z &\longrightarrow \hbar M \ , \qquad M = -S, \cdots, +S \end{aligned}$$

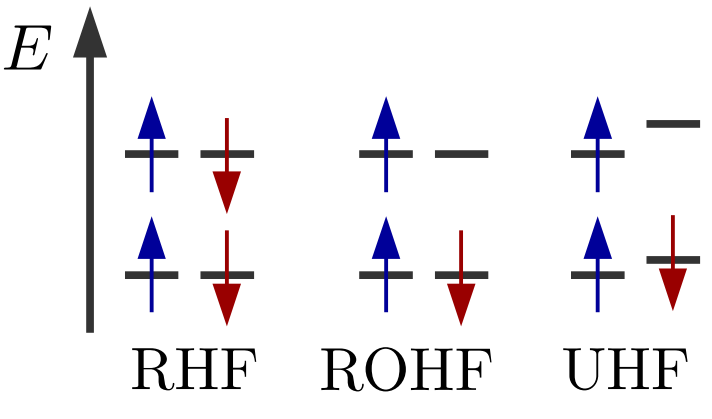
Two possibilities:

- closed shell, this is called **restricted Hartree-Fock (RHF)**.
  In this case M and S are both null (singlet state), and $N_e$ must be even.

$$\psi = \frac{1}{\sqrt{N_e!}}\, det\left|\phi_1(r_1)\overline{\phi}_1(r_2)\phi_2(r_3)\overline{\phi}_2(r_4)\cdots\phi_{N_e/2}(r_{N_e-1})\overline{\phi}_{N_e}(r_{N_e})\right|$$

with $\phi_1(r) = \phi_i(r)\uparrow$ and $\overline{\phi}_1(r) = \phi_i(r)\downarrow$

- restricted open-shell **Hartree-Fock (ROHF)**.
  doubly occupied followed by singly occupied.
  eigenfunction of total $\hat{S}^2$



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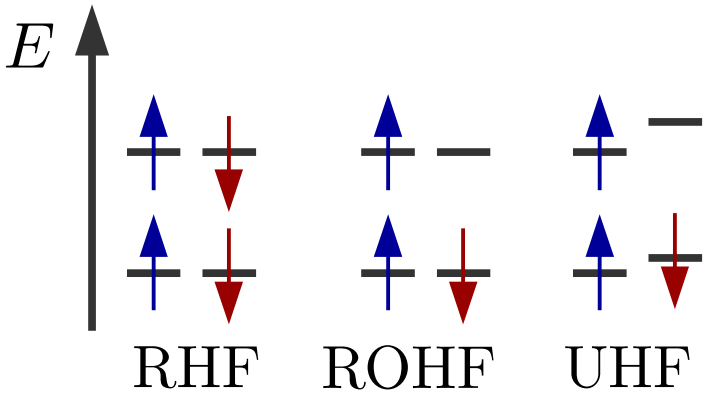
with $\phi_1(r) = \phi_i(r)\uparrow$ and $\overline{\phi}_1(r) = \phi_i(r)\downarrow$

- open shell, **unrestricted Hartree-Fock (UHF)**.
  different orbitals for different spins; coupled eqs.
  In this case S is nonzero, with M in between.



# Hartree-Fock Self Consitent Field (HF-SCF) Method

Assuming that the N-body system does not include interparticle interactions

$$\sum_i \hat{h}_i = \sum_i \hat{T}_i + V(\vec{r}_i)$$

Thus, for this hypothetical case, the exact solution is just a single Slater determinant

$$\psi = \Phi_k$$

and the total energy: $\varepsilon = \sum_i \epsilon_i$

If we allow interparticle interaction this is not enough!

Taking into account the Coulomb interaction between the electrons

$$v(r, r') = e^2/|\vec{r} - \vec{r'}|$$

The energy of the system for a single Slater determinant is written in the HF method as

$$\begin{aligned} \varepsilon_{HF} &= \langle \Phi_k | \hat{H} | \Phi_k \rangle \\ &= \sum_i h_{ii} + \frac{1}{2} \sum_{i,j=1}^{N_e} [\langle \phi_i \phi_j | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | \phi_j \phi_i \rangle] \end{aligned}$$

which must be minimized by finding the optimum spin-orbitals, through the variational procedure

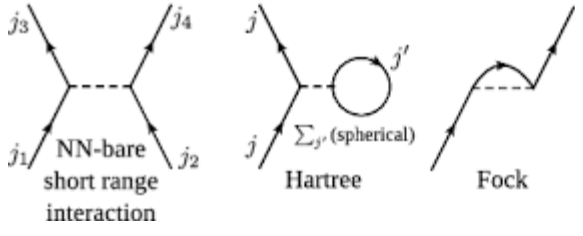
# Hartree-Fock Self Consitent Field (HF-SCF) Method

Applying the variational theory to determine the optimum spatial orbitals, the following one-electron eigenvalue equation may be derived.

$$\hat{f}_i \phi_i = \epsilon_i \phi_i \qquad (1)$$

where the Fock operator is

$$\hat{f}_i = -\frac{1}{2}\nabla_i^2 + \hat{V}_{NN} + \sum_{j=1}^{N_e/2}\left[2\hat{J}_j - \hat{K}_{ij}\right]$$




direct Coulomb (Hartree) potential interaction: $\hat{J}_j(r)\phi_i(r) = \langle\phi_j|\frac{e^2}{|r-r'|}|\phi_j\rangle\phi_i(r)$

exchange potential interaction: $\hat{K}_{ij}(r)\phi_j(r) = \langle\phi_j|\frac{e^2}{|r-r'|}|\phi_i\rangle\phi_j(r)$

Although (1) looks like a Schrödinger equation it is not. Its solution is accomplished self-consistently, as the Coulomb and Exchange operators depends on the orbitals one is seeking.

The total electronic energy is $\varepsilon_{HF} = 2\sum_{i=1}^{N_e/2}\epsilon_i + \sum_{i,j=1}^{N_e/2}(2J_{ij} - K_{ij})$

with $\quad J_{ij} = \langle\phi_i\phi_j|\frac{e^2}{|r-r'|}|\phi_i\phi_j\rangle \qquad K_{ij} = \langle\phi_i\phi_j|\frac{e^2}{|r-r'|}|\phi_j\phi_i\rangle$

# Hartree-Fock-Roothaan Equations

In practice:
A standard method for solving the HF-SCF equations involves expanding the HF orbitals (also called molecular orbitals, MO) as a linear combination of atomic orbitals (LCAO). Therefore the variational procedure is carried out on the coefficients of the expansion

$$\phi_\lambda(r) = \sum_b C_{b\lambda}\varphi_b(r)$$

the HF equations are reformulated as a set of algebraic with respect to the unknown coefficients.

$$\sum_b \left(F_{ab} - \epsilon_\lambda S_{ab}\right) C_{b\lambda} = 0$$

overlap matrix: $S_{ab} = \langle\varphi_a|\varphi_b\rangle$

Fock matrix: $F_{ab} = h_{ab} + \sum_{cd} P_{cd}\left[\langle ac|bd\rangle - \frac{1}{2}\langle ac|bd\rangle\right] = h_{ab} + G_{ab}$

population matrix: $P_{cd} = 2\sum_\lambda^{occ} C^*_{c\lambda}C_{d\lambda}$

Self-consistent procedure:

$$\mathbf{P}^{(0)} \to \mathbf{F}^{(0)} \to \left\{\mathbf{C}^{(0)}_\lambda, \epsilon^{(0)}_\lambda\right\} \to \mathbf{P}^{(1)} \to \mathbf{F}^{(1)} \to \left\{\mathbf{C}^{(1)}_\lambda, \epsilon^{(1)}_\lambda\right\} \to \cdots$$

Total HF energy: $E_{HF} = 2\sum_\lambda \epsilon_\lambda - \frac{1}{2}Tr\left(\mathbf{PG}\right)$

# Electronic Structure Calculation: Density Functional Theory

many-body wavefunction is a complicated beast $\psi(r_1, r_2, \ldots, r_{Ne})$

the ideal situation: use the charge density ρ(r) to obtain the properties of interest.

Earliest approximation by Thomas and Fermi (1927):

$$V_{eN}\left[\rho(r)\right] = -\sum_n \int \frac{eZ_n}{|\vec{r} - \vec{R}_n|}\rho(r)dr \qquad V_{ee}\left[\rho(r)\right] = \frac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{|\vec{r}_1 - \vec{r}_2|}dr_1 dr_2$$

$$T\left[\rho(r)\right] = \frac{3}{10}\left(3\pi^2\right)^{2/3}\int \rho(r)^{5/3}dr$$

degenerate electron gas

unstable for lack of exchange and correlation; in particular $\epsilon_{exch} \gg \epsilon_{corr}$

Slater (1951) derives an approximation for the exchange correlation:

$$E_x\left[\rho(r)\right] = -\frac{9\alpha}{8}\left(\frac{3}{\pi}\right)^{1/3}\int \rho(r)^{4/3}dr$$

with $\alpha$ an adjustable parameter

Not in use anymore, but this work was provocative in its simplicity.

# Density Functional Theory

Hohemberg-Kohn Theorems (1964)

**Existence:**
existence of energy representation via a universal functional; or GS density determines $\hat{H}$.

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## Inhomogeneous Electron Gas*

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(Received 18 June 1964)

This paper deals with the ground state of an interacting electron gas in an external potential $v(\mathbf{r})$. It is proved that there exists a universal functional of the density, $F[n(\mathbf{r})]$, independent of $v(\mathbf{r})$, such that the expression $E\equiv\int v(\mathbf{r})n(\mathbf{r})d\mathbf{r}+F[n(\mathbf{r})]$ has as its minimum value the correct ground-state energy associated with $v(\mathbf{r})$. The functional $F[n(\mathbf{r})]$ is then discussed for two situations: (1) $n(\mathbf{r})=n_0+\tilde{n}(\mathbf{r})$, $\tilde{n}/n_0<<1$, and (2) $n(\mathbf{r})=\varphi(\mathbf{r}/r_0)$ with $\varphi$ arbitrary and $r_0\to\infty$. In both cases $F$ can be expressed entirely in terms of the correlation energy and linear and higher order electronic polarizabilities of a uniform electron gas. This approach also sheds some light on generalized Thomas-Fermi methods and their limitations. Some new extensions of these methods are presented.

# Density Functional Theory

Hohember-Kohn Theorems (1964)

**Existence:**
existence of energy representation via a universal functional; or GS density determines $\hat{H}$.

in DFT language: electrons interact with one another and with an external potential

$$\hat{H} = \underbrace{\left(\hat{T} + V_{ee}\right)}_{\text{intrinsic property of the electronic system}} + V_{ext} = \hat{H}_0 + V_{ext} \qquad V_{ext} \equiv V$$

Proof by contradiction: let us assume that two ***different*** $V_{ext}$ can each be consistent with the ***same nondegenerate*** ground state density ρ

$$\left\{V(r), \psi : E = \langle\psi|\hat{H}|\psi\rangle\right\} \quad \neq \quad \left\{V'(r), \psi' : E' = \langle\psi'|\hat{H}'|\psi'\rangle\right\}$$

$$\rho(r) = \rho'(r)$$

# Density Functional Theory

Starting from the L.H.S.:

$$E < E' + \int \rho'(r)\,[V(r) - V'(r)]\,dr \overset{\rho(r)=\rho'(r)}{\longrightarrow} E < E' + \int \rho(r)\,[V(r) - V'(r)]\,dr \quad (1)$$

Starting from the R.H.S.:

$$E' < E - \int \rho(r)\,[V(r) - V'(r)]\,dr \quad (2)$$

Adding (1) and (2) yields the impossible result: $E + E' < E' + E$

There must be the **UNIQUE** correspondence $\rho(r) \longleftrightarrow V(r)$

Normally $\hat{H} \rightarrow \psi \rightarrow \rho$, but also $\rho \rightarrow \psi\,[\rho(r)] \rightarrow \ E\,[\rho(r)]$

$$E \equiv E\,[\rho] = \underbrace{T\,[\rho] + V_{ee}\,[\rho]}_{\text{universal functional}} + \int \rho(r) V(r) dr$$

(atoms, molecules,solids)

Thus, one can build up the hamiltonian from the ground state density and therefore obtain the ground state wave function

$$\rho \rightarrow V \rightarrow \hat{H} \rightarrow \{\psi_{GS} + all\ other\ "\psi"\}$$

# Density Functional Theory

Hohember-Kohn Theorems (1964)

**Variational Theorem:**
the density obeys a variational principle.

$$E\left[\rho_{GS}\right] \leq \langle \psi' | \hat{H} | \psi' \rangle = E\left[\rho'\right]$$

At least in principle, through the variational principle can find the best ρ without resorting to the infamous many-body Schrödinger equation!

$$\text{Problem: } F_{HK}\left[\rho\right] \equiv T\left[\rho\right] + V_{ee}\left[\rho\right] \text{ remains unknown until now}$$

Approximate procedure was proposed by W. Kohn and L. Sham in 1965.

# Kohn-Sham Self-Consistent Field Method

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## Self-Consistent Equations Including Exchange and Correlation Effects*

W. KOHN AND L. J. SHAM
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(Received 21 June 1965)

From a theory of Hohenberg and Kohn, approximation methods for treating an inhomogeneous system of interacting electrons are developed. These methods are exact for systems of slowly varying or high density. For the ground state, they lead to self-consistent equations analogous to the Hartree and Hartree-Fock equations, respectively. In these equations the exchange and correlation portions of the chemical potential of a uniform electron gas appear as additional effective potentials. (The exchange portion of our effective potential differs from that due to Slater by a factor of $\frac{2}{3}$.) Electronic systems at finite temperatures and in magnetic fields are also treated by similar methods. An appendix deals with a further correction for systems with short-wavelength density oscillations.

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{eff}(r,[\rho])\right]\varphi_\lambda(r) = \epsilon_\lambda\varphi_\lambda(r)$$

with

$$V_{eff}(r,[\rho]) = V(r) + \frac{\delta V_{ee}[\rho]}{\delta\rho} + \left(\frac{\delta T[\rho]}{\delta\rho} - \frac{\delta T_0[\rho]}{\delta\rho}\right)$$

# Kohn-Sham Self-Consistent Field Method

Main approximation: use the non-interacting electron gas as a building block, and approximate the rest.

Thus

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(r) V(r) dr$$

is rewritten as

$$E[\rho] = T_0[\rho] + V_{eff}[\rho]$$

with all the unknown correlations included in the exchange-correlation energy functional that goes into the one-body effective potential $V_{eff}$.

The eigenvalue equation for a fictitious system electrons that interact through a one-body potential determined by the actual electronic density.

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V_{eff}(r,[\rho])\right]\varphi_\lambda(r) = \epsilon_\lambda \varphi_\lambda(r)$$

with

$$V_{eff}(r,[\rho]) = V(r) + \frac{\delta V_{ee}[\rho]}{\delta\rho} + \left(\frac{\delta T[\rho]}{\delta\rho} - \frac{\delta T_0[\rho]}{\delta\rho}\right)$$

***The eigenvalue equation must be solved through the self-consistent field (SCF) procedure.***

# Kohn-Sham Self-Consistent Field Method

Thus

$$E[\rho] = T[\rho] + V_{ee}[\rho] + \int \rho(r) V(r) dr$$

is rewritten as

$$E[\rho] = \left(T_0[\rho] + E_H[\rho] + \int \rho(r) V(r) dr\right) + E_{XC}[\rho]$$

with all the unknown correlations are included in the exchange-correlation energy functional

$$E_{XC}[\rho] \equiv V_{ee}[\rho] - E_H[\rho] + T[\rho] - T_0[\rho] = \Delta V_{ee} + \Delta T$$

which is a universal functional.

$T_0$ and $E_H$ are big and easy to calculate; $E_{XC}$ is expected to be smaller.

$E_H$ is the **known** Hartree energy

$$E_H[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|\vec{r}_1 - \vec{}_2|} dr_1 dr_2$$

$V_{XC}$ is the ***unknown*** exchange-correlation potential

$$V_{XC}(r) = \frac{\delta E_{XC}[\rho]}{\delta \rho(r)}$$

# Kohn-Sham Self-Consistent Field Method

The Kohn-Sham single-particle eigenvalue equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \sum_n^{N_{nuc}} \frac{eZ_n}{|r-R_n|} + \int \frac{\rho(r')}{|r-r'|} + V_{XC}\right]\varphi_\lambda = \epsilon_\lambda \varphi_\lambda$$

and $\quad V_{XC} = \dfrac{\delta E_{XC}}{\delta \rho}$ .

The single-particle orbitals comprise the Slater-determint eigenfunction

$$\sum_i^{N_e} \hat{h}_i^{KS} |\varphi_1 \varphi_2 \cdots \varphi_{N_e}\rangle = \sum_i^{N_e} \epsilon_i |\varphi_1 \varphi_2 \cdots \varphi_{N_e}\rangle$$

The *Kohn-Sham matrix* $K_{ab}$ is comparable with the *Fock matrix* $F_{ab}$.

$$K_{ab} = \left\langle \varphi_a \left| -\frac{\hbar^2}{2m}\nabla^2 - \sum_n^{N_{nuc}} \frac{eZ_n}{|r-R_n|} + \int \frac{\rho(r')}{|r-r'|} + V_{XC} \right| \varphi_b \right\rangle$$

So far DFT is ***exact***, although **unsoluble**.

# Local Density Approximation (LDA)

DFT is, in principle, an exact theory, as long as we know $V_{XC}$

The LDA, introduced by KS is the simplest approximation method, which has been surprisingly successful.

In general one writes:

$$E_{XC}\left[\rho(r)\right] = \int \rho(r)\ \varepsilon_{XC}\left[\rho(r)\right] dr$$

separating the contributions from exchange and correlation

$$\varepsilon_{XC}\left[\rho(r)\right] = \varepsilon_{X}\left[\rho(r)\right] + \varepsilon_{C}\left[\rho(r)\right]$$

Because:

- usually $\varepsilon_X \gg \varepsilon_C$
- $\varepsilon_X$ is known exactly for the homogeneous electron system

For the jellium system

$$\varepsilon_x\left[\rho\right] = -\frac{9}{8}\alpha\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3} \qquad \alpha = \frac{2}{3}\ \text{for LDA}$$

# Local Density Approximation (LDA)

- The correlation part is much more complicated
- use results from Quantum Monte Carlo by Ceperley-Alder to fit $\varepsilon_C$ for various densities.

LDA method:

discretize in a grid: $\rho(r) \to \rho_i$ so that $n_i = \int_{\mathcal{V}_i} \rho(r) dr = \rho_i \mathcal{V}_i$

$\rho_i$ must be single valued, but otherwise can be wildly ill-behaved (cusps at the nuclei positions)

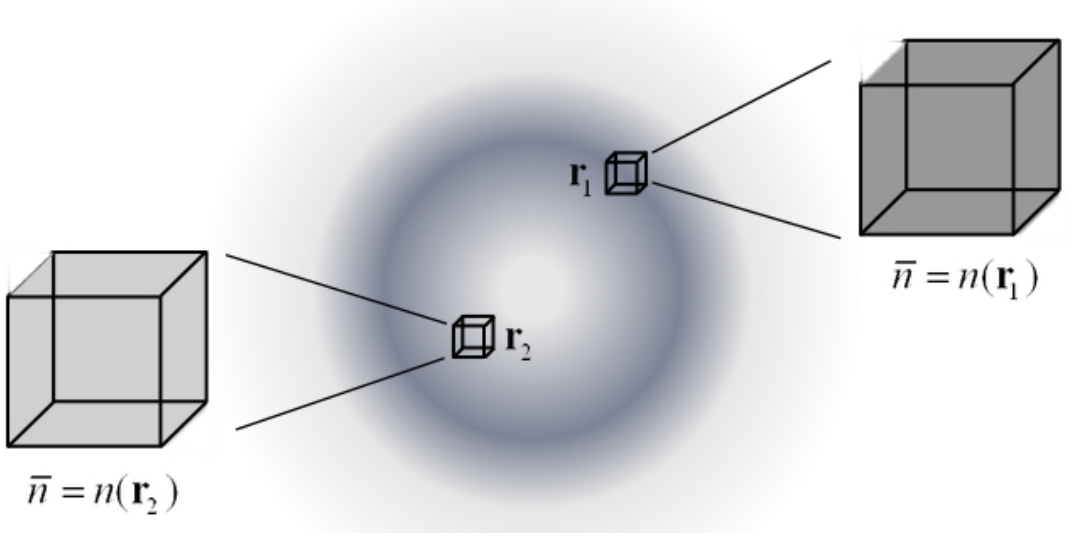
Perform a grid integration to obtain

$$E_{XC}^{LDA}[\rho] \approx \sum_i \underbrace{\varepsilon_{XC}(\rho_i)}_{\text{for the uniform gas}} \rho_i \mathcal{V}_i$$

and

$$\begin{aligned} V_{XC}^{LDA} &= \frac{\partial}{\partial \rho(r)} \int \rho(r') \varepsilon_{XC}(\rho(r')) dr' \\ &= \varepsilon_{XC}(\rho(r)) + \rho(r) \left( \frac{\partial \varepsilon_{XC}(\rho)}{\partial \rho} \right) \Bigg|_{\rho=\rho(r)} \end{aligned}$$

# Local Density Approximation (LDA)





http://web.missouri.edu/~ullrichc/

# Density Gradient Corrections

- LDA is a local DFT
- beyond that there is gradient corrected semi-local DFT
  for instance, GGA is Generalized Gradient Approximation

$$\varepsilon_{XC}^{GGA}\left[n_{\uparrow}, n_{\downarrow}\right] = \int \varepsilon_{XC}\left(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}\right) \rho(\mathbf{r})\; d^3r$$

semi-local: $r + \partial/\partial r$ versus $(r, r')$

# Self-Interaction in DFT

- In the LDA method every electron interacts with its own electron desity which is physically unacceptable.
- In particular, the sum of Hartree, $E_H$ , and exchange-correlation, $E_{XC}$ , energies for a Hidrogen atom (single electron) should be zero (cancel out), but it does not happen in general for DFT functionals.

$$\left\langle \psi \left| \sum_{i<j}^{N_e} \frac{1}{r_{ij}} \right| \psi \right\rangle = \frac{1}{2}\int\int \frac{\rho(r_1)\rho(r_2)}{|\vec{r}_1 - \vec{}_2|} dr_1 dr_2 + \frac{1}{2}\int\int \frac{\rho(r_1)h(r_1, r_2)}{|\vec{r}_1 - \vec{}_2|} dr_1 dr_2$$

- $h(r_1,r_2)$ is the pair distribution (hole) function.
- there is not self-interaction in HF since Coulomb and exchange integrals cancel out by construction.
- hybrid functionals (B3LYP, PBE0, HSE, *etc.*) incorporate exact exchange from HF.

# HF x DFT : In summary

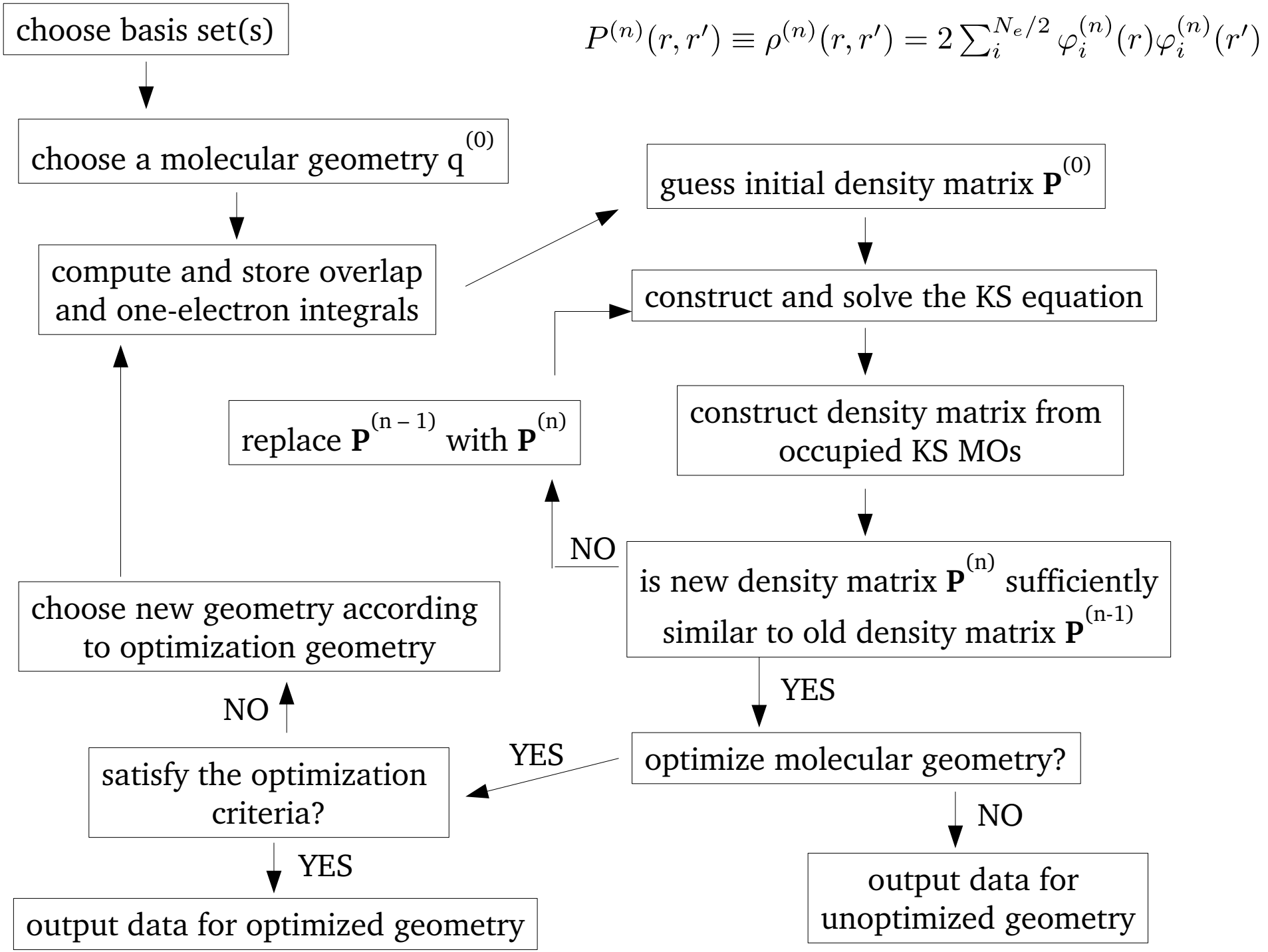
- HF: effective potential is nonlocal.
- DFT: effective potential is local (LDA) . GGA is semi-local approximation.

- HF: exchange interaction is treated exactly; correlation effects not present at all.
- DFT: both exchange and correlation are included, at some level of approximation.

- HF: deliberately approximate theory, whose equations can be solved exactly (for small systems at least).
- DFT: exact theory whose equations can only be solved approximately.

- *If the same basis are used,* the KS matrix, $K_{ab}$ , is the same as *Fock matrix,* $F_{ab}$ , except for the exchange-correlation parts.
- historically, this made easy the transition from HF to DFT.

# Flow chart of a KS-SCF procedure




$$P^{(n)}(r,r') \equiv \rho^{(n)}(r,r') = 2\sum_{i}^{N_e/2} \varphi_i^{(n)}(r)\varphi_i^{(n)}(r')$$

# Computational Cost

Scaling: Hartree-Fock

$$E_{HF} = \sum_i 2\epsilon_i - \sum_{i,j}(2J_{ij} - K_{ij})$$

$\epsilon_i \longrightarrow$ Eigenvalues $\longrightarrow$ Diagonalization $\longrightarrow \mathcal{O}(N^3)$

$J_{ij},\ K_{ij} \longrightarrow$ Coulomb, exchange integrals $\longrightarrow \mathcal{O}(N^4)$

$$J_{ij} = \int \phi_i^*(r_1)\phi_j^*(r_2)\,\frac{1}{|r_1 - r_2|}\,\phi_i(r_1)\phi_j(r_2)$$

$$K_{ij} = \int \phi_i^*(r_1)\phi_j^*(r_2)\,\frac{1}{|r_1 - r_2|}\,\phi_j(r_1)\phi_i(r_2)$$

Diagonalization:

$$\mathbf{F}C_i = \epsilon_i \mathbf{S}C_i$$

Generally $\longrightarrow$ $\mathcal{O}(N^3)$

Prefactor depends on algorithm

# Computational Cost

Two-eletron four-center integrals:

$$J_{ij} = \int\int d\mathbf{r_1} d\mathbf{r_2}\ \phi_i^*(r_1)\phi_j^*(r_2)\,\frac{1}{|r_1 - r_2|}\,\phi_i(r_1)\phi_j(r_2)$$

$\phi(r)$ are molecular orbitals which can be written in terms of atom centered orbitals:

$\phi_i(r) = \sum_a C_{ai}\chi_i(r)$ , so that

$$J_{ij} = \sum_{a,b,c,d} \Omega^{ij}_{abcd} \int\int d\mathbf{r_1} d\mathbf{r_2}\ \chi_a^*(r_1)\chi_b^*(r_2)\,\frac{1}{|r_1 - r_2|}\,\chi_c(r_1)\chi_d(r_2)$$

Life is hard:

There are formally $\mathcal{O}(N^4)$ of these integrals for a basis set of size $N$

But in practice... truncation:

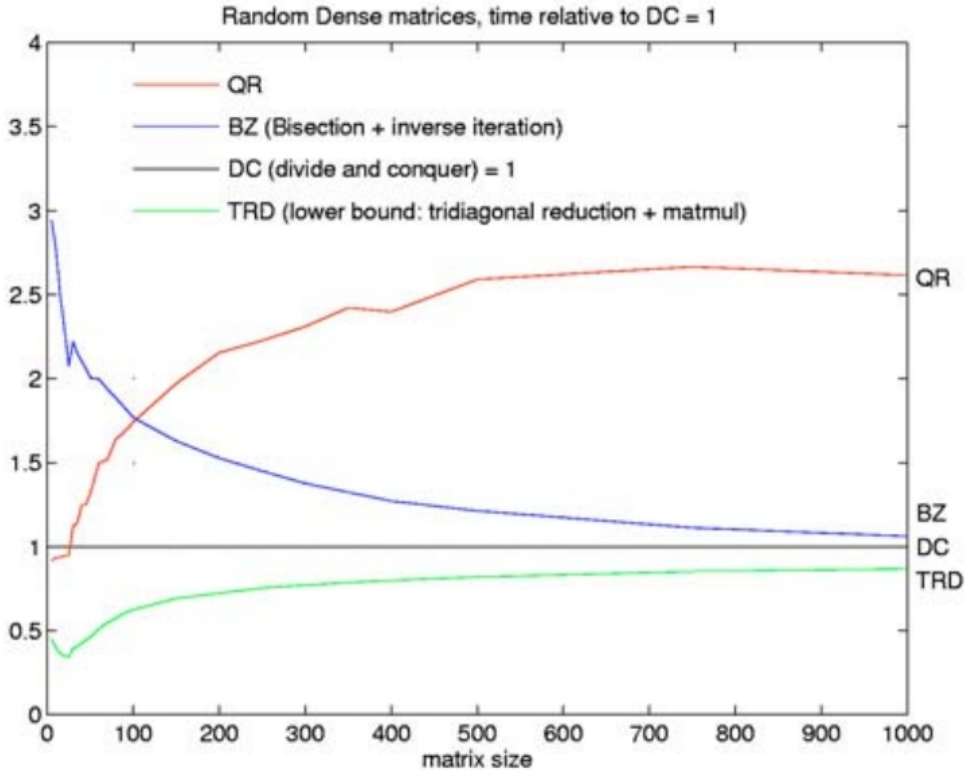
for a suitable choice of localized orbitals the number of nonnegligible integrals grows as $\mathcal{O}(N^2)$

unless $S_{ij}$ is non-negligible.

# Computational Cost

LAPACK (driver routines)

| *Method* | *Routine* |
|---|---|
| Divide & Conquer | xSYEVD / xSYGVD |
| Tridiagonal QR | xSYEV / xSYGV |
| Bisection and Inverse Iteration | xSYEVX / xSYGVX |
| Relatively Robust Representations | xSYEVR |




James W. Demmel,
*Applied Numerical Linear Algebra*,
pg. 238

# Computational Cost

Diagonalization:

Iterative methods (subspace methods):

General idea: **Minimize residual vector**

Iterate through subspace

$$r = (\mathbf{A} - \lambda \mathbf{I})v \quad \longrightarrow \quad \mathcal{O}(n^2)$$

Power method
Lanczos
Arnoldi
...their variants
…and many more

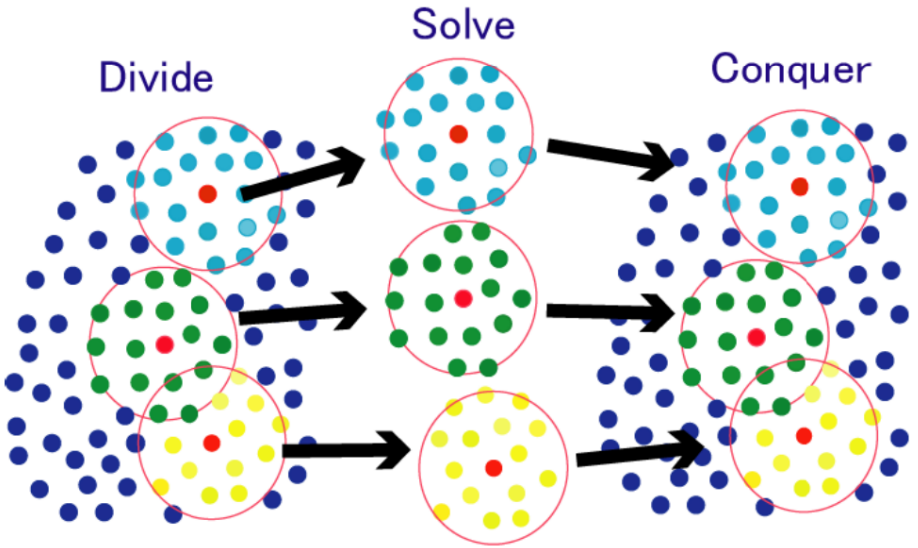
→ Active research area

# Computational Cost

Diagonalization:

Iterative methods: ***O(N)*** methods

Based on physical approximations: **Quantum locality**

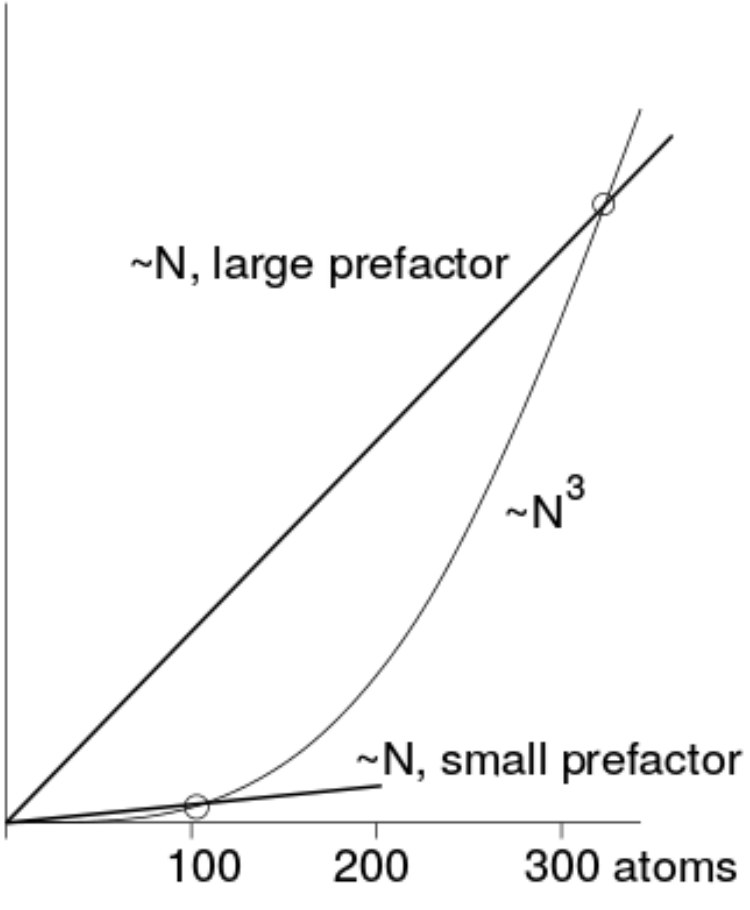



http://www.openmx-square.org/tech_notes/Krylov_WS08.pdf

# Computational Cost

Diagonalization:

Iterative methods: ***O(N)*** methods

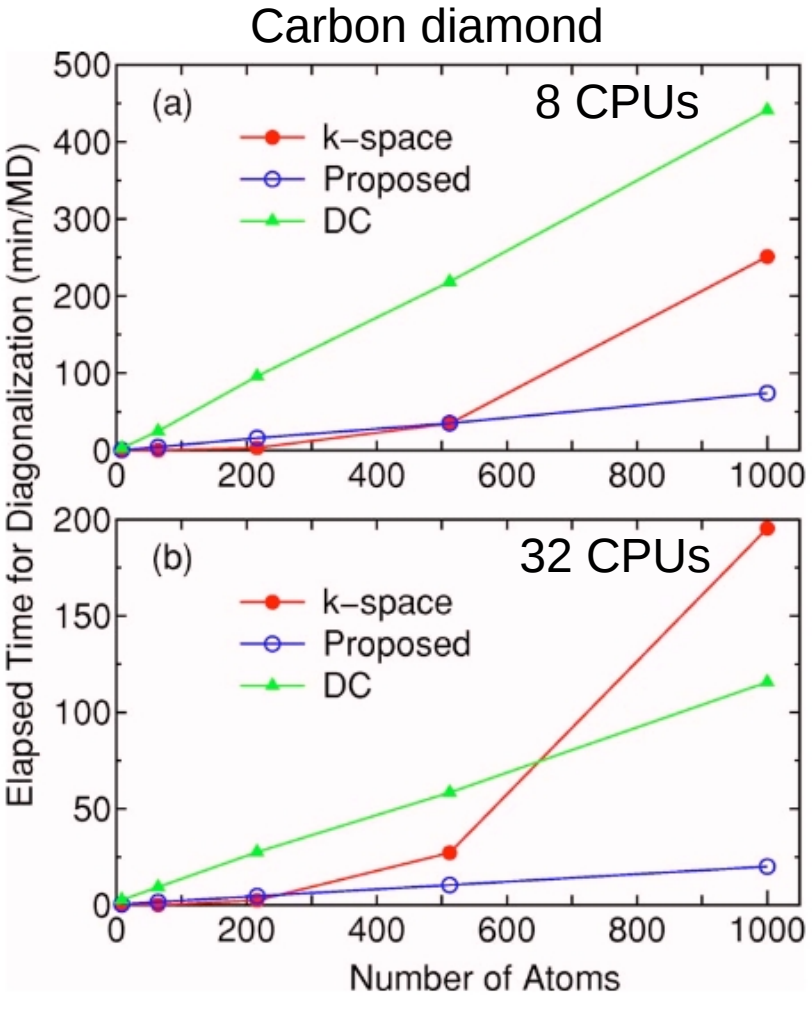



Prefactor may be relevant !

# Computational Cost

Diagonalization:

Iterative methods: ***O(N)*** methods




k-space → Direct method (which?)
Proposed → Krylov
DC → Divide & Conquer

**O(N) Krylov-subspace method for large-scale ab initio electronic structure calculations**

Taisuke Ozaki

Phys. Rev. B 74, 245101 (2006)

# Computational Cost

## Various linear scaling methods

Wannier functions (WF)
Density matrix (DM)
} × {
Variational (V)
Perturbative (P)

At least four kinds of linear-scaling methods can be considered as follows:

| WF+V | WF+P | DM+V | DM+P |
|---|---|---|---|
| Orbital minimization by Galli, Parrinello, and Ordejon | Hoshi Mostofi | Density matrix by Li and Daw | **Krylov subspace** Divide-conquer Recursion Fermi operator |

http://www.openmx-square.org/tech_notes/Krylov_WS08.pdf