Fundamentals of Density Functional Theory

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Outline: Part 1

- First-principles electronic structure calculations
- Why and what is “density functional theory (DFT)”?
  - non-interacting *v*-representability
  - “Kohn-Sham particles” — self-consistent solutions
- Concept of exchange-correlation energy functional
  - “local density approximation (LDA)”
  - exchange-correlation hole
  - generalized gradient approximation (GGA)
  - hybrid functional

First-principles electronic structure calculations

What do you mean by “first principles”?

Dictionary:
“A ***first principle*** is a basic proposition or assumption that cannot be deduced from any other proposition or assumption.”

Dictionary:
Ab initio: “starting from the beginning”

In practice:
“**Ab initio**” or “**first principles**” means
“starting from the self-consistent electronic structure based on the density functional theory.”

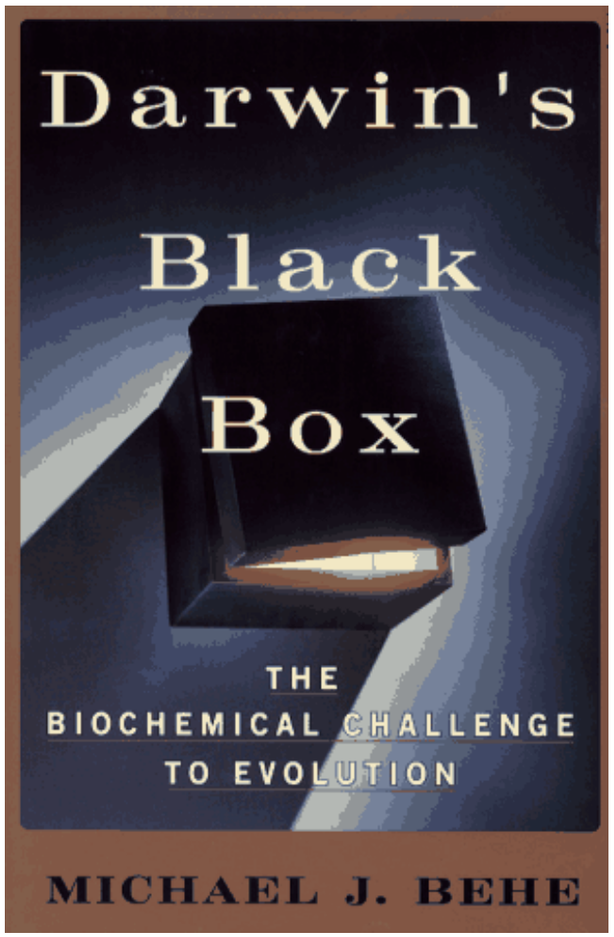
N-body Schrodinger's equation

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 + \sum_i v(\mathbf{r}_i) + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\right]\Psi_n(\{\mathbf{r}_i\}) = E_n\Psi_n(\{\mathbf{r}_i\})$$

“The underlying laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that exact applications of these laws lead to equations which are too complicated to be soluble.”

— P.A.M. Dirac (1929)

Some people tend to think that DFT is a *computing* "**black box**":

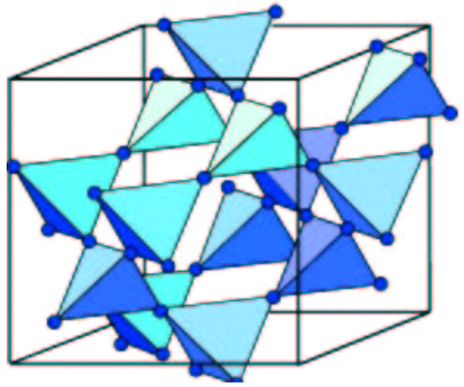


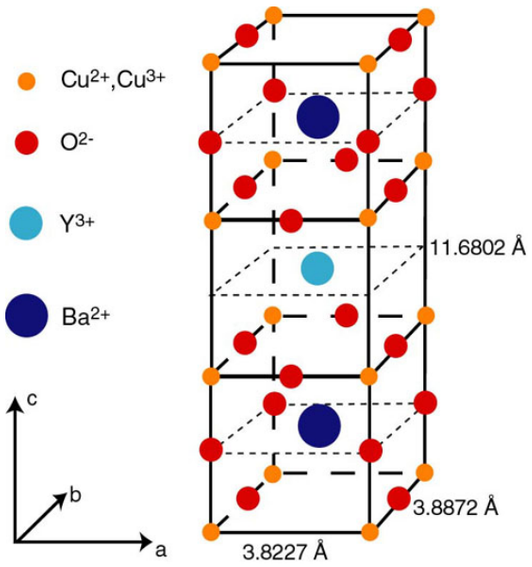
A microscopic
picture
provided by
…
"**computations**"
based on
first-principles.

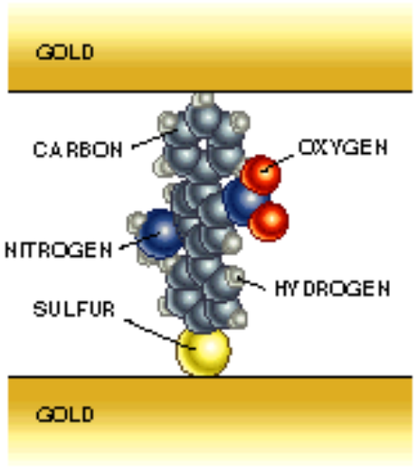
What DFT really is …

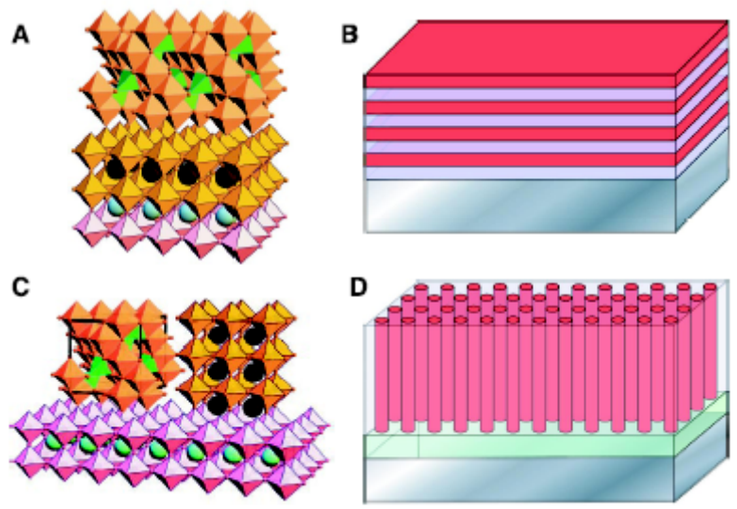
a mean field description of real materials:

- the detailed information on atoms, molecules, and other physical constituents as well as their geometrical structures are crucial in understanding the physics
- more important in nano-scale physics where the individual atoms and molecules contributes more









Why and What is “density functional theory (DFT)”?

N-body Schrodinger's equations

$$\left[-\frac{1}{2}\sum_{i=1}^{N_e}\nabla_i^2+\sum_{i=1}^{N_e}v(\mathbf{r}_i)+\frac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi_{N_e}(\{\mathbf{r}_k\})=E_{N_e}\Psi_{N_e}(\{\mathbf{r}_k\})$$

Once we solve these equations …

we can obtain whatever physical properties by calculating the expectation values of observables

$$\langle\hat{O}_\alpha\rangle=\langle\Psi_N|\hat{O}_\alpha|\Psi_N\rangle$$

But, practically, solving these equations …

is ***limited*** to a few cases …, *still* with some approximations!

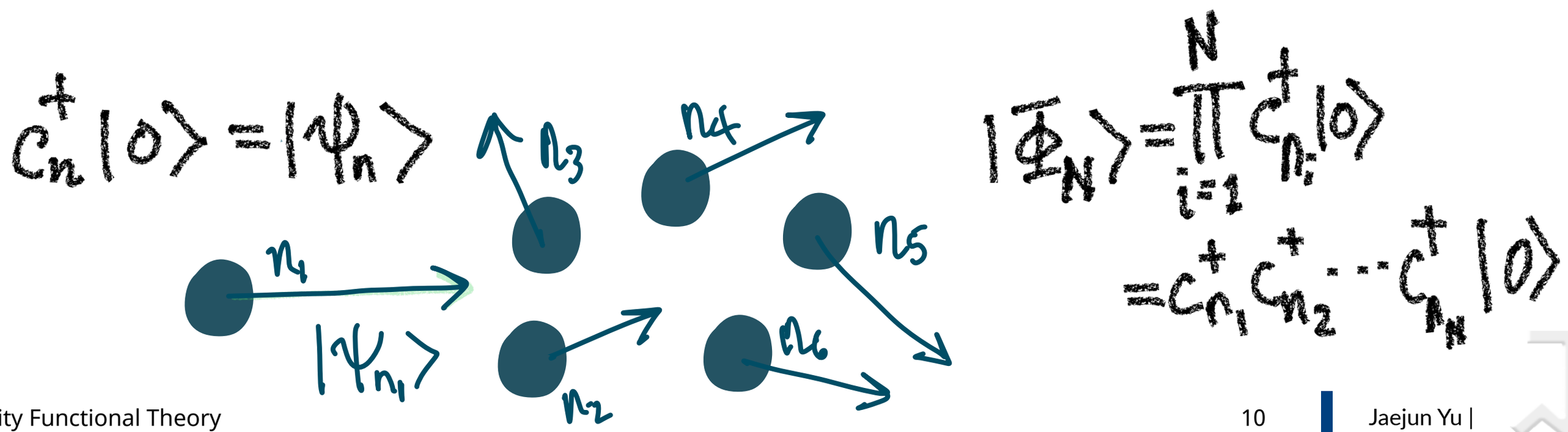
One-body systems

One-particle Schrodinger's equation:

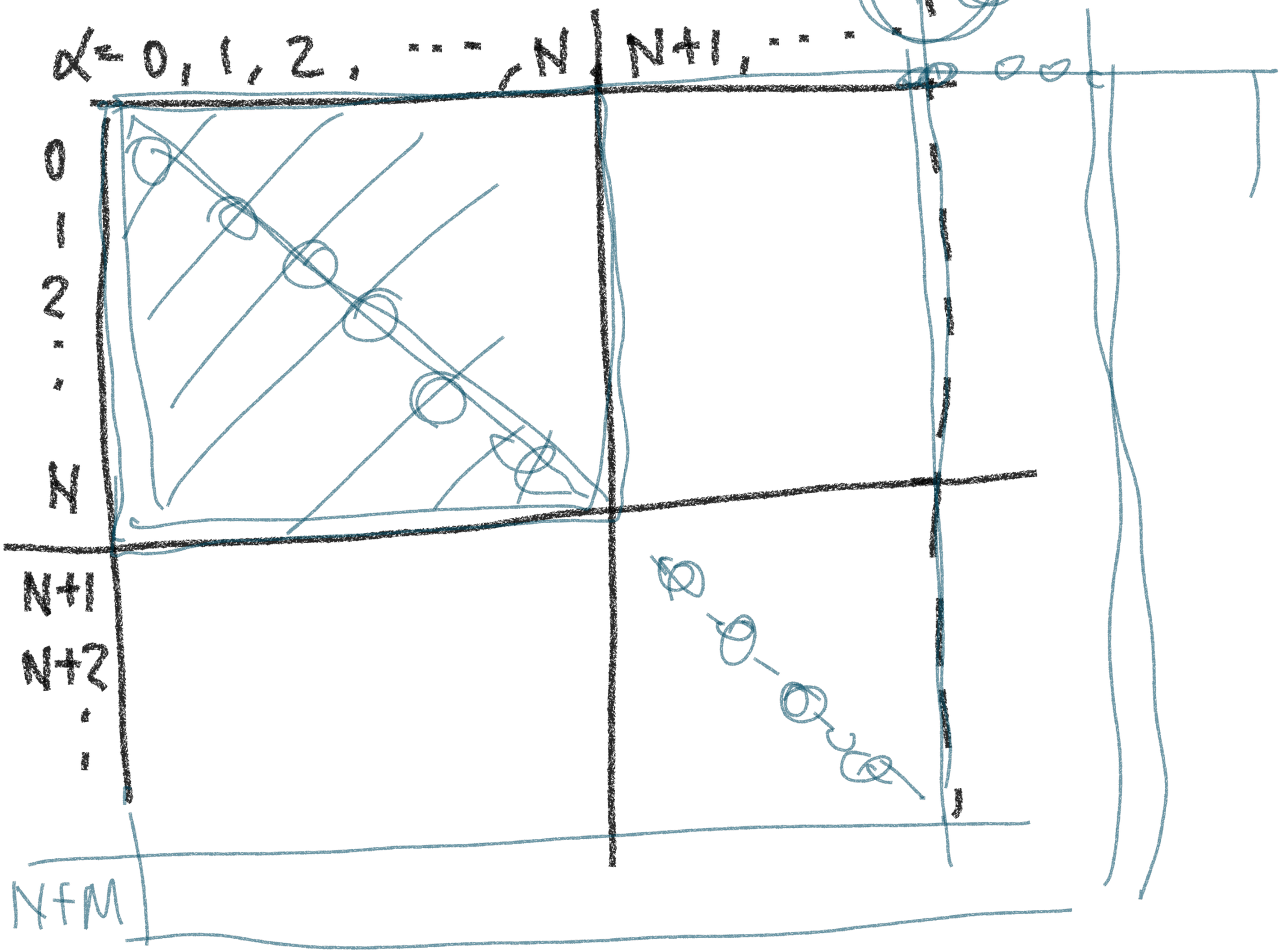
$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right]\psi_n(\mathbf{r}) = \varepsilon_n\psi_n(\mathbf{r})$$

where the eigenstate can be represented by

$$\psi_n(\mathbf{r}) = \sum_{\alpha=1}^{M} c_n(\alpha)\phi_\alpha(\mathbf{r})$$



$$\hat{H}|\phi_\alpha\rangle = \varepsilon|\phi_\alpha\rangle$$



N-body systems

$|\Psi_{N,n}\rangle$

$$\left[-\frac{1}{2}\sum_{i=1}^{N_e}\nabla_i^2+\sum_{i=1}^{N_e}v(\mathbf{r}_i)+\frac{1}{2}\sum_{i\neq j}^{N_e}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\right]\Psi_{N_e}(\{\mathbf{r}_k\})=E_{N_e}\Psi_{N_e}(\{\mathbf{r}_k\})$$

where the N-particle state with energy $E_{N,\kappa}$ can be represented by

$$E_{N,\kappa}\Rightarrow \qquad |\Psi_{N,\kappa}\rangle=\sum_{\{n_i\}}C_{N,\kappa}(\{n_i\})\,|\Phi_{N,\{n_i\}}\rangle$$

Here, note that $|\Phi_{N,\{n_i\}}\rangle$ corresponds to the Slater determinant of $\{\psi_{n_i}(\mathbf{r}_i)\}$ N-orbitals.

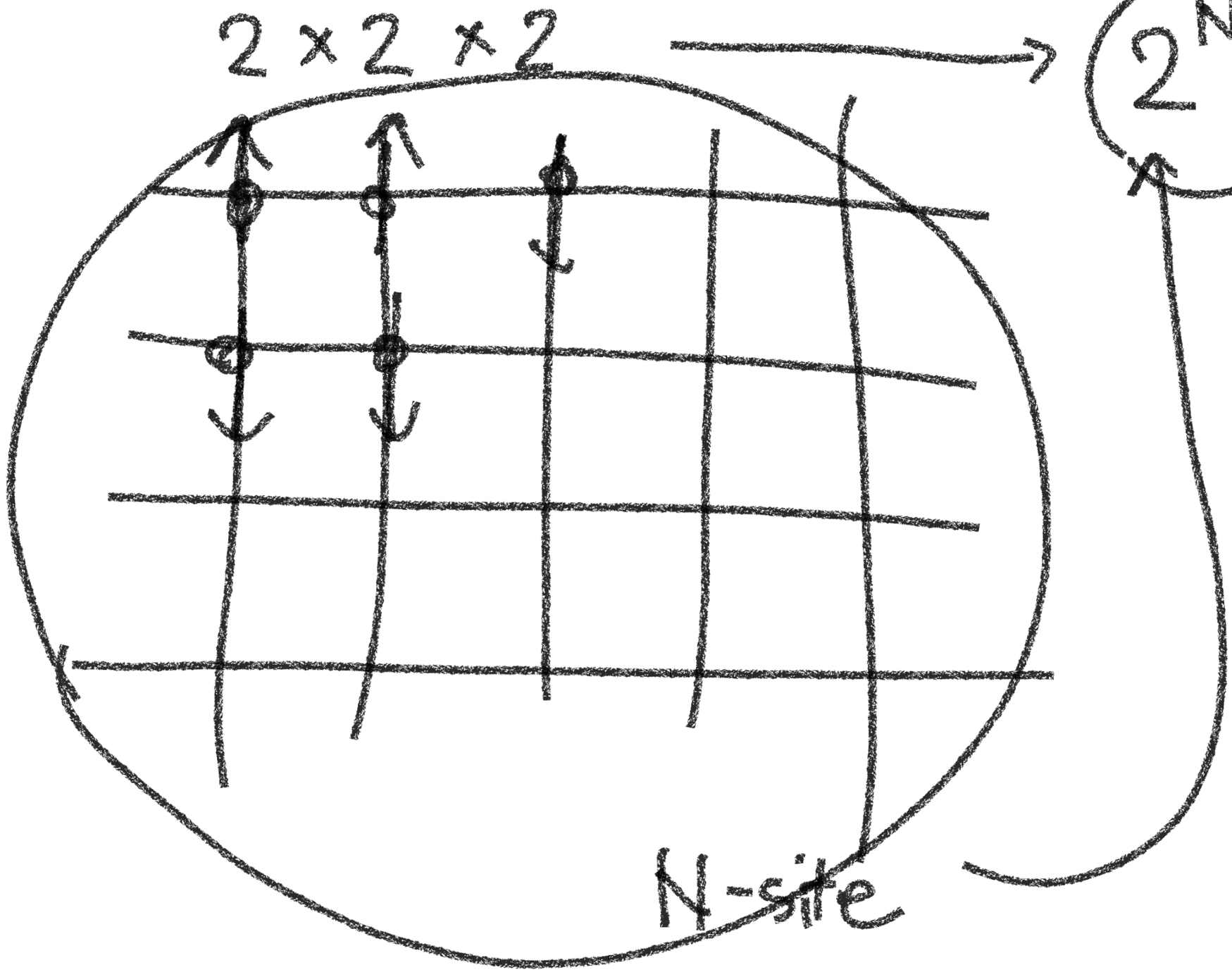
$$|\Phi_{N,\{n_i\}}\rangle=\prod_{i=1}^{N}c_{n_i}^{+}|0\rangle$$

Dimensional reduction via DFT

- Suppose that $\alpha_i = 1,2,\ldots,M$ of the *i-th* particle residing at the N independent lattice site. Then the total number of available states $\{\Phi_{\{\alpha_i\}}\}$ becomes $M^N \sim N^N \sim N!$

$N!$-dimensional space vs. 3d functional space

$M^N \times M^N$ matrix vs. $N \times N$ matrix





$|\Psi_\sigma\rangle$

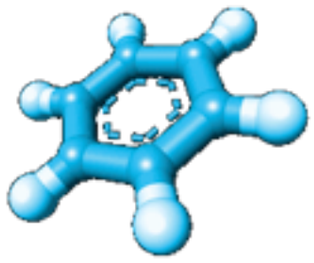
$\sigma = \{\sigma_1, \sigma_2, \cdots \sigma_N\}$

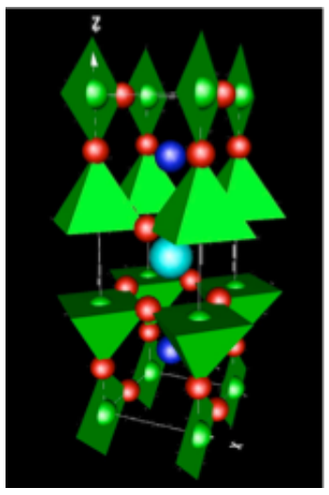
2^N

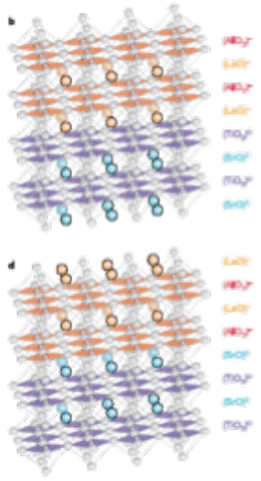
Example:
Configuration Interactions in Quantum Chemistry Calculations?

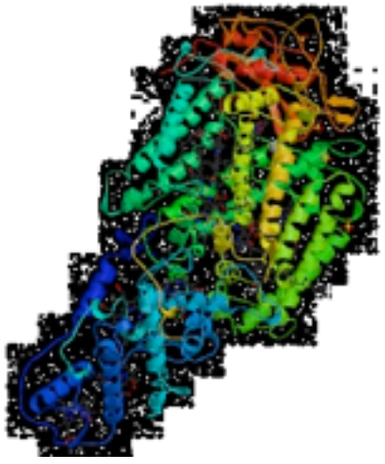
$$|\Psi\rangle = C_0|\Phi_0\rangle + \sum_{ra} c_a^r|\Phi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs}|\Phi_{ab}^{rs}\rangle + \sum_{r<s<t,a<b<c} c_{abc}^{rst}|\Phi_{abc}^{rst}\rangle + \cdots,$$

$$\mathbf{H} = \begin{array}{c} \langle\Phi_0| \\ \langle S| \\ \langle D| \\ \langle T| \\ \langle Q| \\ \vdots \end{array} \begin{bmatrix} \langle\Phi_0|H|\Phi_0\rangle & & & & & \cdots \\ 0 & \langle S|H|S\rangle & & & & \cdots \\ \langle D|H|\Phi_0\rangle & \langle D|H|S\rangle & \langle D|H|D\rangle & & & \cdots \\ 0 & \langle T|H|S\rangle & \langle T|H|D\rangle & \langle T|H|T\rangle & & \cdots \\ 0 & 0 & \langle Q|H|D\rangle & \langle Q|H|T\rangle & \langle Q|H|Q\rangle & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}.$$









Maybe, all right for this small molecule.
But, not for any larger systems of interest …

Basic strategy is …

$|\Psi_{N,n}\rangle$

Interacting *N*-particles

$$|\Psi_N\rangle = \sum_{\{\alpha_i\}} C_{\{\alpha_i\}} |\Phi_N\{\alpha_i\}\rangle$$

$|\tilde{\Psi}_{N,n}\rangle$

Ensemble of non-interacting N-particles

$$|\tilde{\Psi}_N\rangle \cong \prod_{i=1}^{N} \tilde{c}^{\dagger}_{\alpha_i} |0\rangle + \delta |\tilde{\Psi}_N\rangle$$

utilizing solutions of 1-particle Schrodinger's equations, which we can solve exactly or numerically!

$$\left[-\frac{1}{2}\nabla^2 + v(\mathbf{r})\right] \tilde{\psi}_n(\mathbf{r}) = \varepsilon_n \tilde{\psi}_n(\mathbf{r})$$

$$\tilde{\psi}_n(\mathbf{r}) = \sum_{\alpha=1}^{M} c_n(\alpha) \tilde{\phi}_\alpha(\mathbf{r})$$

Hohenberg-Kohn Theorem

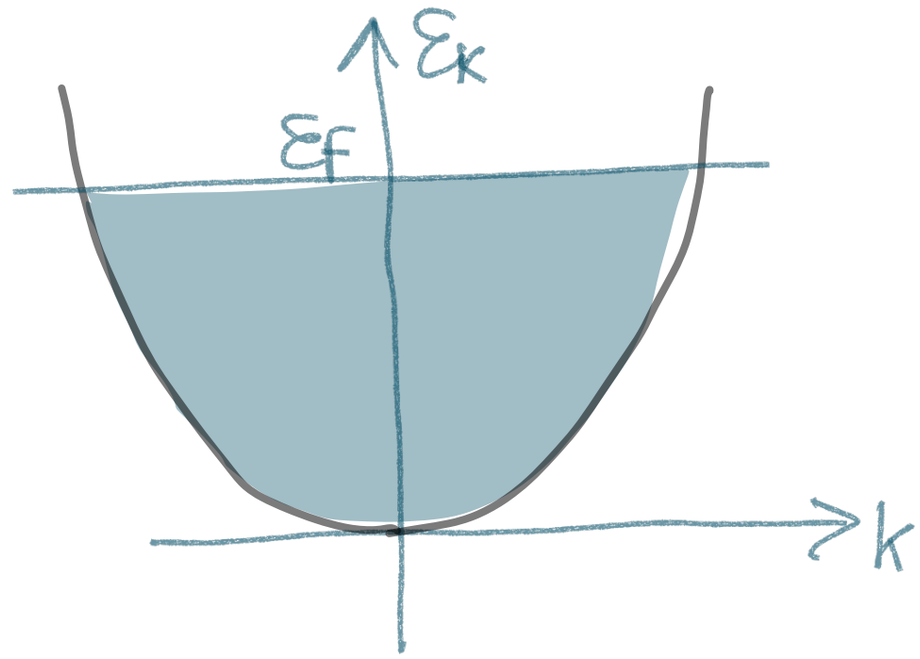
- The exact many-body wavefunction (and all the ground state properties) of the interacting many-body system is determined by the charge density $n(\mathbf{r})$
- There exists a unique universal functional of the density, $F[n(\mathbf{r})]$, independent of the external potential $v(\mathbf{r})$, such that

$$E_v = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + F[n(\mathbf{r})]$$

has its minimum value at the correct ground-state energy associated with $v(\mathbf{r})$.

$$n(\mathbf{r}) = \langle \Psi_o | \hat{\psi}^+(\mathbf{r}) \hat{\psi}(\mathbf{r}) | \Psi_o \rangle \Leftrightarrow |\Psi_o\rangle$$

Example: free electrons in a box with a constant potential v_o



- Fermi Energy: $\varepsilon_F = k_F^2/2 + v_o$
- Fermi wave vector: $k_F = \sqrt{2(\varepsilon_F - v_o)}$
- Number density:

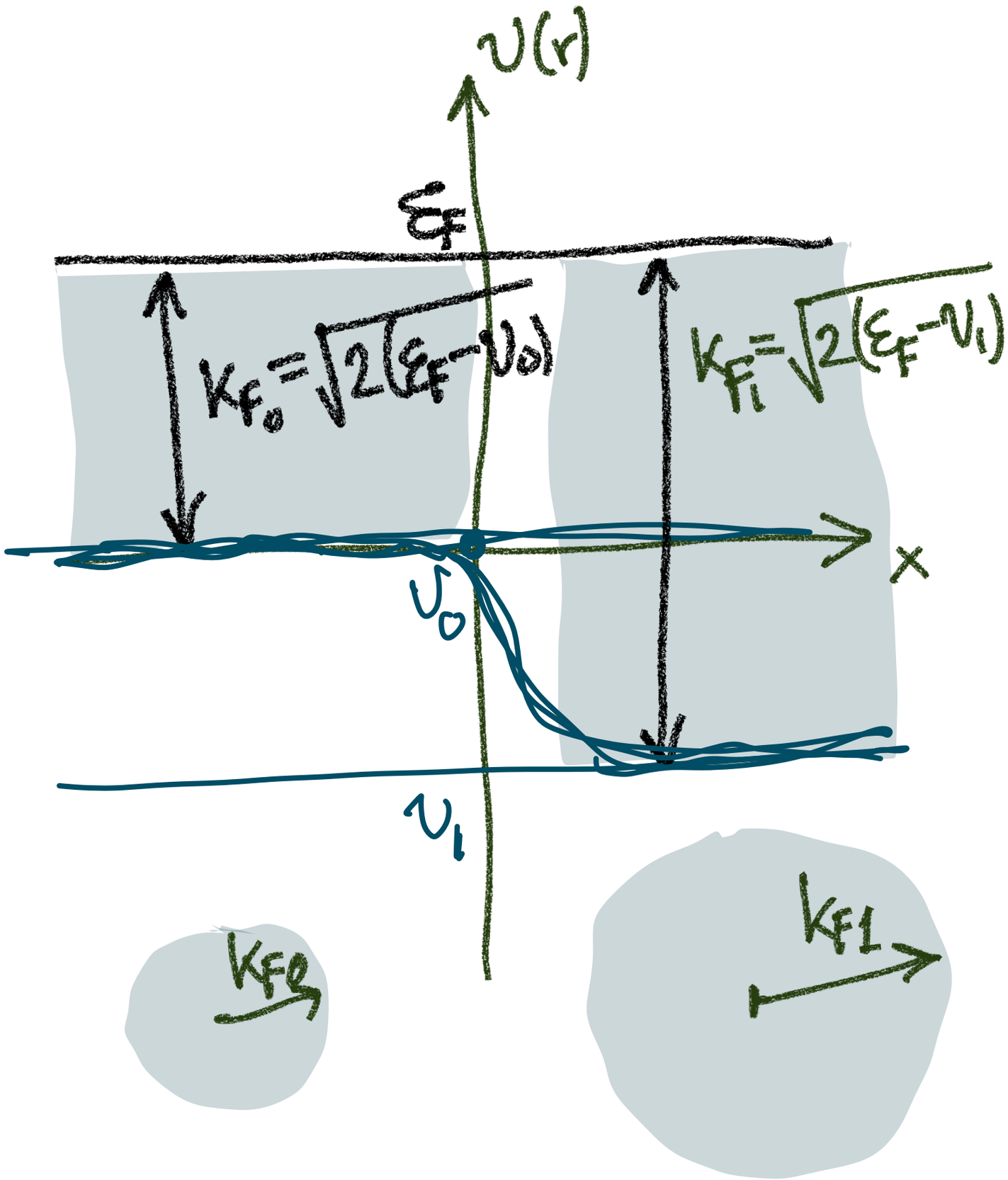
$$n = \frac{k_F^3}{3\pi^2}$$

$$n(\mathbf{r}) = n(v_o) = \frac{1}{3\pi^2}\left(2(\varepsilon_F - v_o)\right)^{3/2}$$

- Total energy:

$$\frac{E_o}{V} = \frac{3}{5}\frac{k_F^2}{2}n + v_o n = \frac{3}{10}(3\pi^2)^{2/3}n^{5/3} + v_o n$$

Note: Total energy E_o is a function of n, which is in turn a function of v_o.



- Kinetic energy

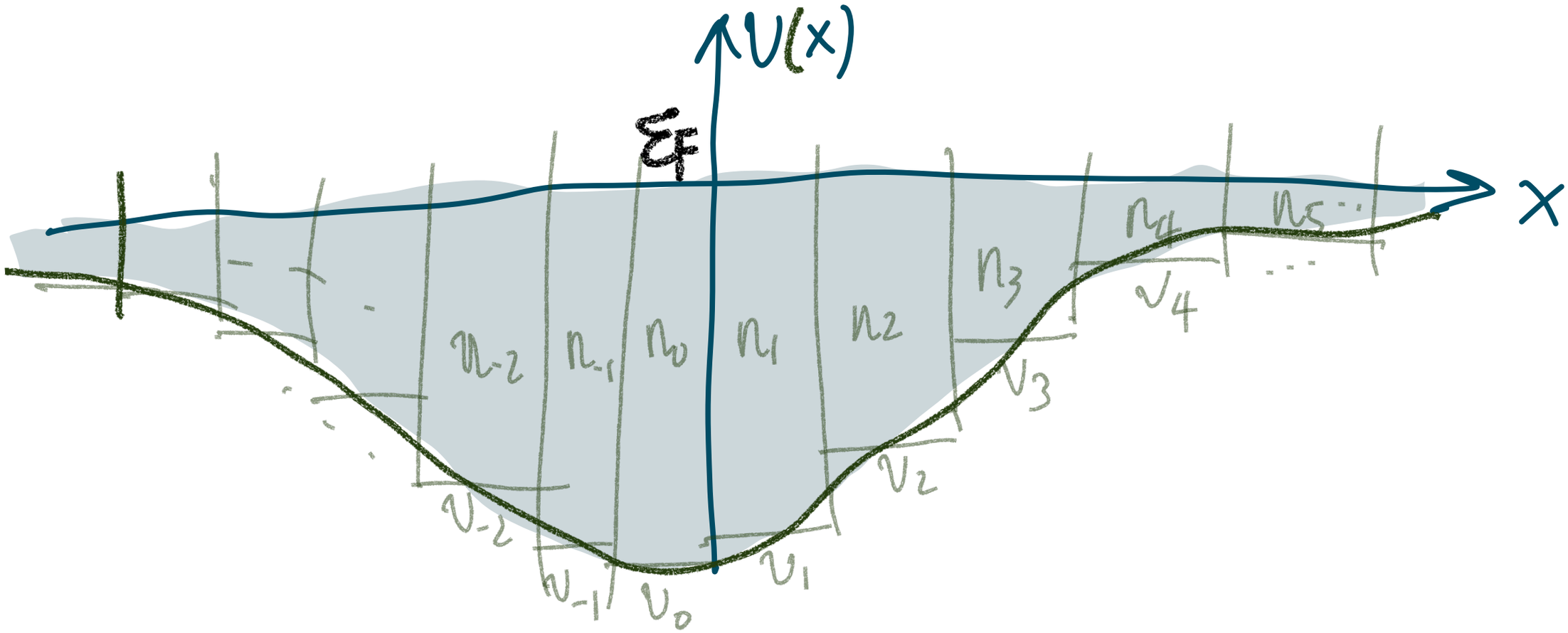
$$\left(\frac{3}{5}\frac{k_{F_i}^2}{2} \times n_i\right) = \frac{3}{10}(3\pi^2)^{2/3} n_i^{5/3}$$

for the region of potential V_i

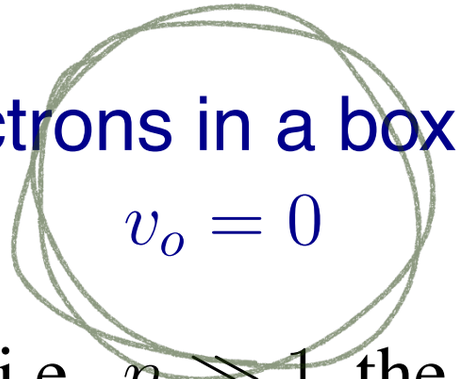
Thomas-Fermi Theory

Description of Kinetic Energy for inhomogeneous systems as a function of local density $n(\mathbf{r})$:

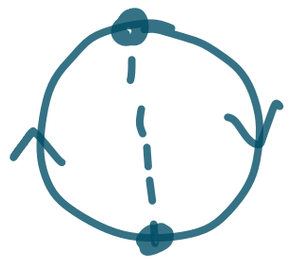
$$T = \frac{3}{10}(3\pi^2)^{2/3}\int [n(\mathbf{r})]^{5/3} d\mathbf{r}$$



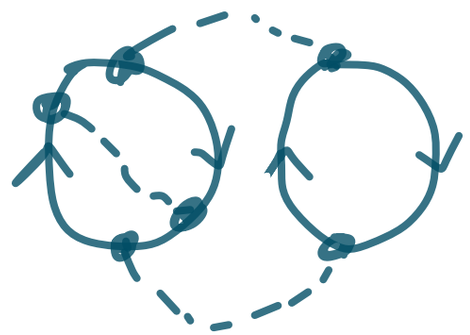
Example: interacting electrons in a box with a constant potential



For a large density system, i.e., $n \gg 1$, the total energy of the interacting electron gas can be expressed in a perturbation expansion of the parameter $(1/k_F) \propto (1/n^{1/3})$:

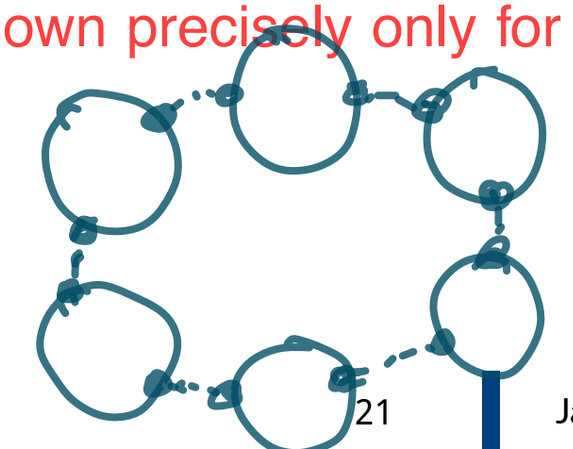


$$E = E_o(1 + A\frac{1}{k_F} + B\frac{1}{k_F^2} + ...)$$
$$= T_o - A'n^{4/3} + B'n + C'\ln(n) + ...$$



- T_o : kinetic energy
- $E_x = -A'n^{4/3}$: exchange energy
- $E_c = B'n + C'\ln(n) + ...$: correlation energy

The form of the E_{xc} exchange-correlation energy is known precisely only for the homogeneous interacting electron gas (jellium) system.



v-representability

$$E_v[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r}) + F[n(\mathbf{r})]$$

$$n(\mathbf{r}) = \langle \Psi_N | \hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r}) | \Psi_N \rangle \Longleftrightarrow v(\mathbf{r})$$

$v(\mathbf{r})$ → $\mathcal{H}|\Psi_0\rangle = E_0|\Psi_0\rangle$ → $|\Psi_0\rangle$ → $n(\mathbf{r}) = \langle \Psi_0 | \hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r}) | \Psi_0 \rangle$ → $n(\mathbf{r})$ → $v(\mathbf{r})$

one-to-one mapping

$v(\mathbf{r})$ → $|\Psi_N\rangle$ → $n(\mathbf{r})$ → $v(\mathbf{r})$

Finding "$n(\mathbf{r})$" for the ground state?

Applying the variational method for the minimum $E_v[n]$ under the constraint $\int n(\mathbf{r})d\mathbf{r} = N$:

$$\frac{\delta}{\delta n(\mathbf{r})}\left[E_v - \mu\left(\int n(\mathbf{r})d\mathbf{r} - N\right)\right] = 0$$

$$\frac{\delta F[n(\mathbf{r})]}{\delta n(\mathbf{r})} + v(\mathbf{r}) = \mu$$

n-representability

Introducing a new set of extra variational "parameters" $\{\phi_i(\mathbf{r})|i = 1, 2, ..., N\}$ for the density $n(\mathbf{r})$:

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

$\phi_i(\mathbf{r})$ $(i = 1, ..., N)$ are the orbitals of **fictitious** (non-interacting fermion) N-particles moving under the **effective** potential v_{eff}:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right] \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r})$$

— Kohn-Sham Equations

With the number-of-particles constraint:

$$\int |\phi_i(\mathbf{r})|^2 d\mathbf{r} = 1$$

the total energy functional can be written by

$$E_v[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{ion}$$

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^{N} \langle \phi_i | \nabla^2 | \phi_i \rangle$$

$$E_H[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$E_{xc}[n] = \int \varepsilon_{xc}[n] n(\mathbf{r}) d\mathbf{r}$$

$$E_{ion} = \frac{1}{2}\sum_{ij}\frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

Taking the **variation** with respect to $\phi_i(\mathbf{r})$:

$$\frac{\delta}{\delta\phi_i^*(\mathbf{r})}\left[E_v[n] - \sum_{i=1}^{N}\epsilon_i\left(\int|\phi_i(\mathbf{r})|^2 d\mathbf{r} - 1\right)\right] = 0$$

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int\frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}d\mathbf{r}' + v_{xc}(\mathbf{r})$$

“Kohn-Sham particles” — self-consistent solutions

$$E_v[n] = T_s[n] + E_H[n] + E_{xc}[n] + \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{ion}$$

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r})\right]\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r})$$

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2$$

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + v_{xc}(\mathbf{r})$$

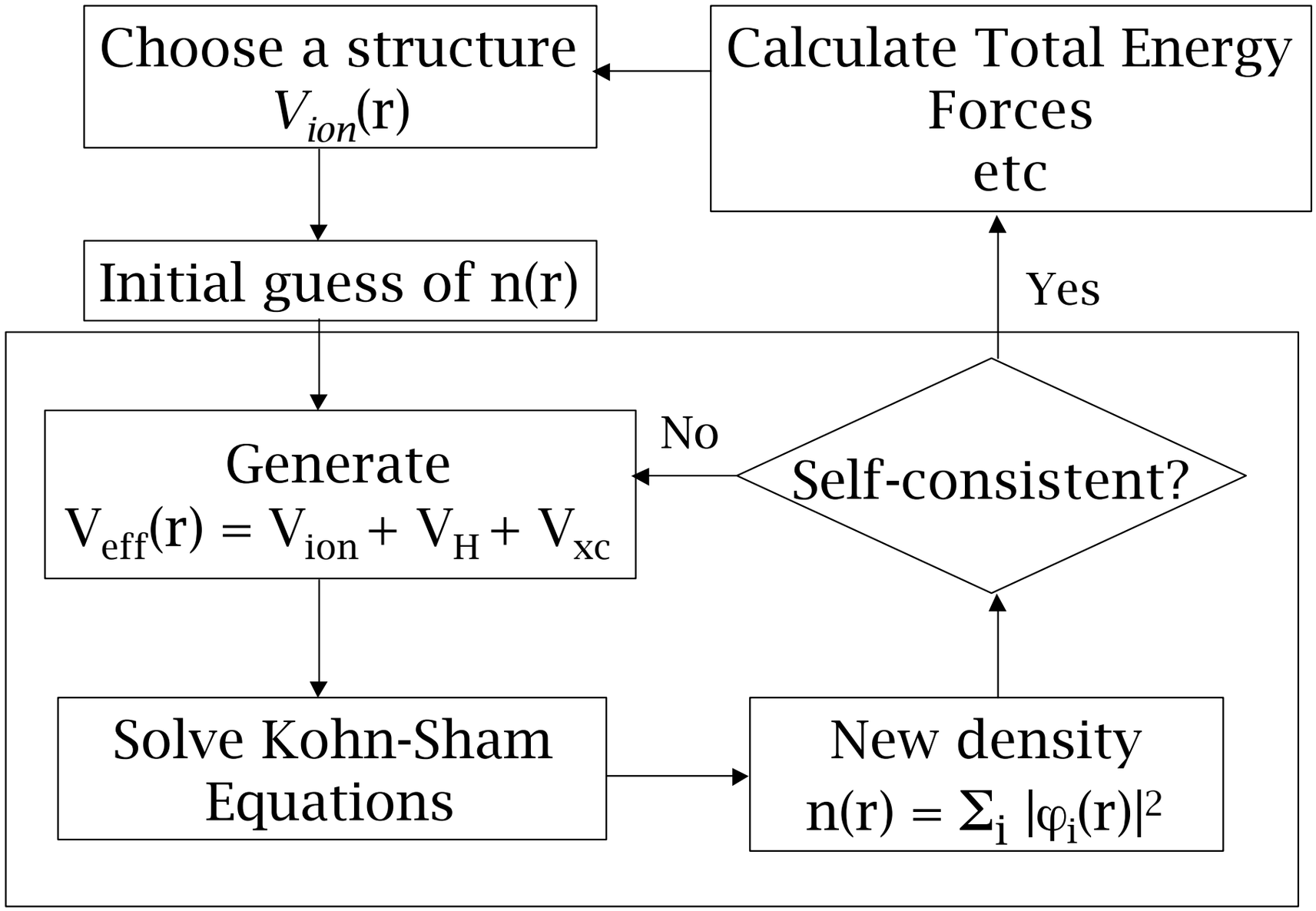
$$T_s[n] = -\frac{1}{2}\sum_{i=1}^{N}\langle\phi_i|\nabla^2|\phi_i\rangle$$

$$E_H[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$$

$$E_{xc}[n] = \int \varepsilon_{xc}[n]n(\mathbf{r})d\mathbf{r}$$

$$E_{ion} = \frac{1}{2}\sum_{ij}\frac{Z_iZ_j}{|\mathbf{R}_i-\mathbf{R}_j|}$$

Self-Consistent Calculation Algorithm



non-interacting *v*-representability

$$E_v[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r}) + F[n(\mathbf{r})]$$

$$n_0(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2 \quad \overset{1:1}{\Longleftrightarrow} \quad n(\mathbf{r}) = \langle \Psi_N | \hat{\psi}^+(\mathbf{r})\hat{\psi}(\mathbf{r}) | \Psi_N \rangle$$

True for $\hat{\mathcal{H}}_0 = \sum_{\alpha\beta} t_{\alpha\beta} c_\alpha^\dagger c_\beta$ systems

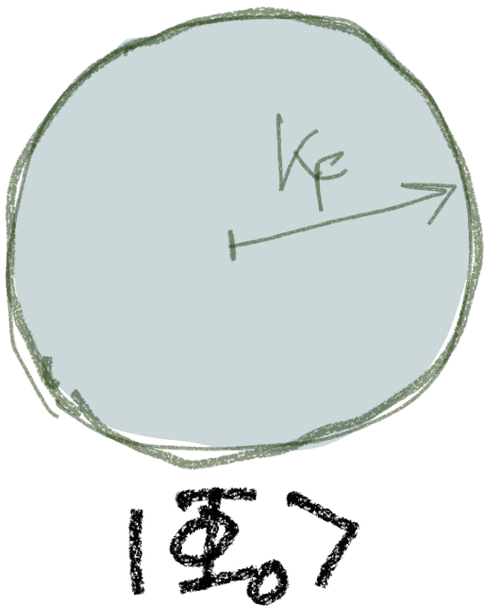
But, for interacting systems, it may fail.

e.g., $\hat{\mathcal{H}} = \sum_{\alpha\beta} t_{\alpha\beta} c_\alpha^\dagger c_\beta + U_{\alpha\beta} \hat{n}_\alpha \hat{n}_\beta$

- M. Levy, Phys. Rev. A 26, 2100 (1982).
- M. E. Casida and M. Huix-Rotlant, Annu. Rev. Phys. Chem. 63, 287 (2012).

$$|\Phi_0\rangle = \prod_{k<k_F} c_k^\dagger |0\rangle$$

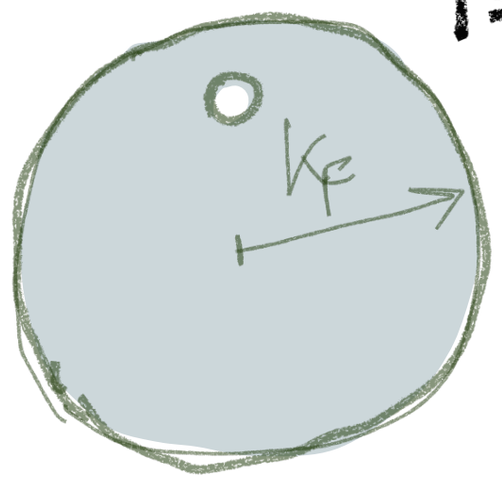
$$\hat{H}_0 = \sum_k \varepsilon_k^0 c_k^\dagger c_k$$

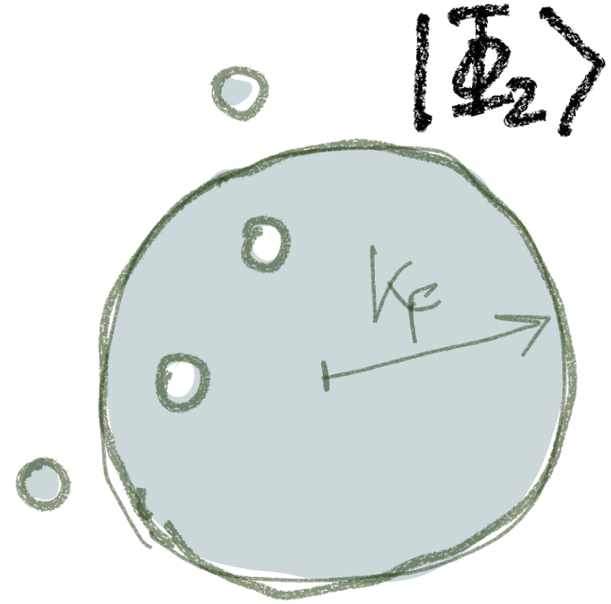


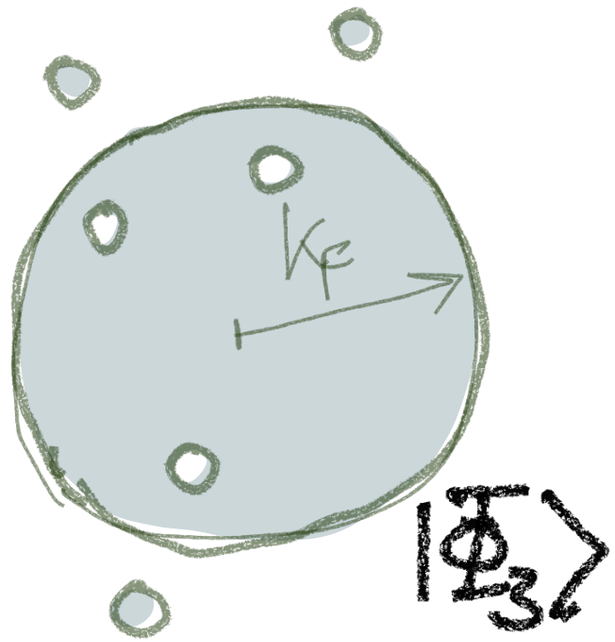
$$H_1 = \sum_{\substack{k,q \\ k'}} V_q c_{k+q}^\dagger c_k c_{k'-q}^\dagger c_{k'}$$

$$|\Psi\rangle = c_0|\Phi_0\rangle + c_1|\Phi_1\rangle + c_2|\Phi_2\rangle + \dots$$

$$|\Phi_1\rangle = c_{k_1}^\dagger c_{k_1+q} |\Phi_0\rangle$$



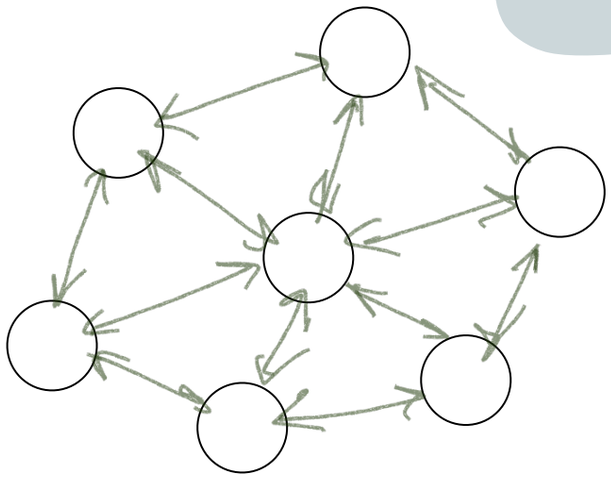


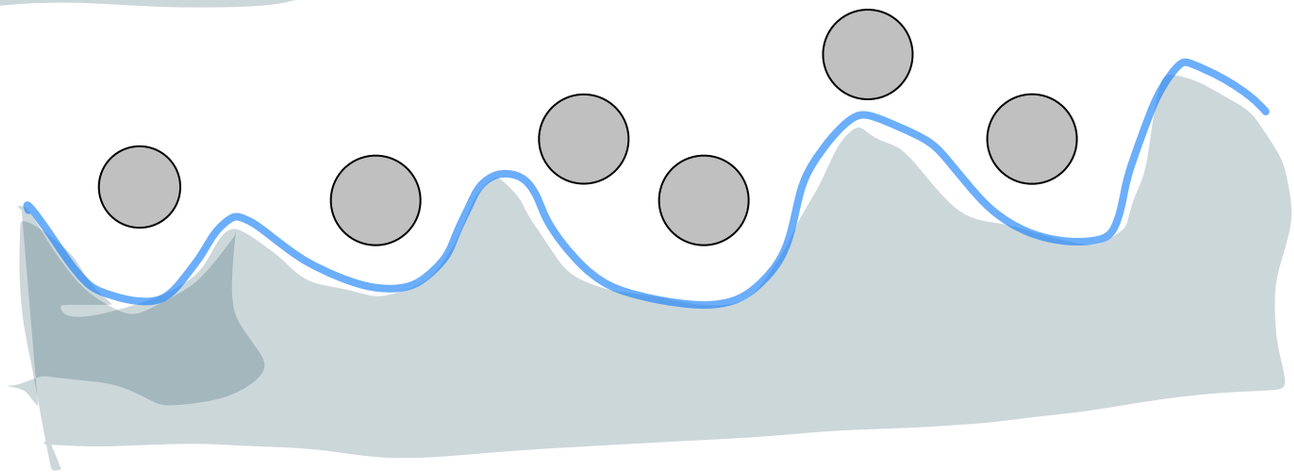


Kohn-Sham equations …

Mapping the $n(\mathbf{r})$ of “interaction N-electrons” into that of fictitious particle moving under an effective potential, i.e., $n_0(\mathbf{r})$:

$$n(\mathbf{r}) = n_0(\mathbf{r})$$





interacting electrons

$$n(\mathbf{r})$$

non-interacting electrons
under an effective potential

$$n_0(\mathbf{r}) = \sum_i |\phi_i(\mathbf{r})|^2 f(\epsilon_i)$$

Concept of exchange-correlation energy functional

“local density approximation (LDA)”

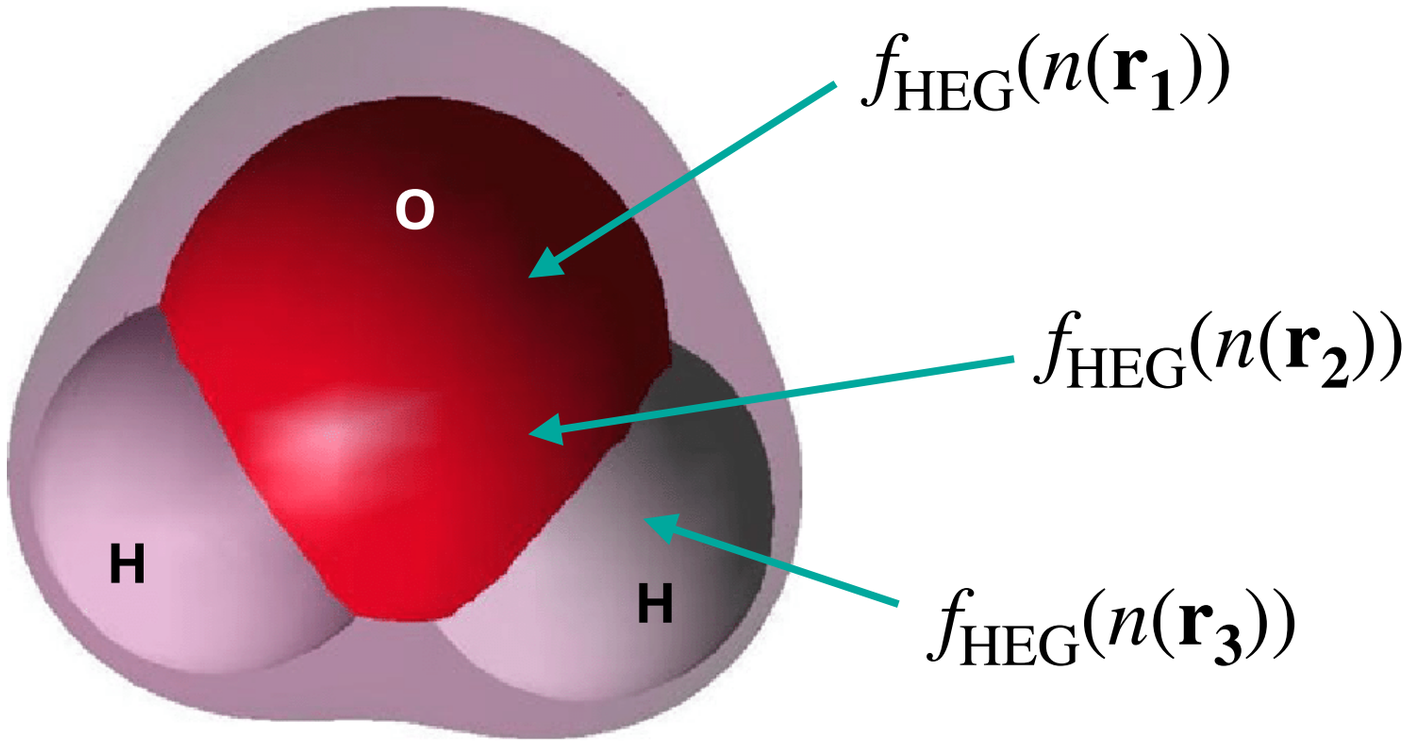
- Exchange-correlation potential of the homogeneous electron gas (HEG) *is **a function of density**, **not a functional***!

$$F_{\mathrm{HEG}}[n(\mathbf{r})] = f_{\mathrm{HEG}}(n_0) \cdot V,$$

where the density function is a constant $n(\mathbf{r}) = n_0$ for all $\mathbf{r}$.

- For the slowly varying density,

$$F[n(\mathbf{r})] \approx F^{\mathrm{LDA}} = \int f_{\mathrm{HEG}}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r} \approx \sum_i f_{\mathrm{HEG}}(n(\mathbf{r_i}))n(\mathbf{r_i})\Delta v(\mathbf{r_i})$$



$$E_{\text{xc}}^{\text{inhomo}}[n] \approx \int d\mathbf{r}\ n(\mathbf{r})\varepsilon_{\text{xc}}^{\text{homo}}(n(\mathbf{r}))$$

$$V_{\text{xc}}^{\text{LDA}}(\mathbf{r}) \approx \frac{\delta E_{\text{xc}}^{\text{homo}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}$$

Assuming $\varepsilon_{xc}[n] = \varepsilon_{xc}(n(\mathbf{r}))$,

$$v_{xc}(\mathbf{r}) = \frac{d}{dn(\mathbf{r})}\left(n\varepsilon_{xc}(n(\mathbf{r}))\right)$$

The n-dependence of ε_{xc} can be obtained as accurately as possible via Quantum Monte Carlo Calculations of Ceperley-Alder Form parameterized by Perdew and Zunger.

$E_{xc}[n(\mathbf{r})]$ in KS-formalism is …

not *just* “exchange and correlation”

HK formalism: $E_v[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + T[n] + E_{ee}[n]$

KS formalism: $E_v[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + E_{ion} + T_s[n] + E_H[n] + E_{xc}[n]$

$E_H[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$: classical ‘Coulomb’ interaction energy

$T[n] \neq T_s[n] = -\frac{1}{2}\sum_{i=1}^{N}\langle\phi_i|\nabla^2|\phi_i\rangle$ **: Kinetic energy of “fictitious” KS-particles**

$$E_{xc}[n] = (T[n] - T_s[n]) + (E_{ee}[n] - E_H[n])$$

ΔT includes some kinetic contributions

Adiabatic connection:
scaling of electron–electron interactions

$\lambda = 0$ **— fictitious system of non-interacting electrons**

density $n(\mathbf{r})$ remains unchanged!

$$\mathcal{H} = \mathcal{H}_s + \lambda V_{ee} + W_\lambda[n]$$

- $\mathcal{H}_s$: Kohn-Sham Hamiltonian
- λV_{ee}: Electron-electron interactions
- $W_\lambda[n]$: Local restoring potential to adjust $n(\mathbf{r})$

$\lambda = 1$ **— real system of interacting electrons**

- J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974).
- M. Levy, J. Chem. Phys. 104, 1989 (1996).

exchange-correlation hole

$$E_{ee} = \langle \Psi_N | \left\{ \frac{1}{2} \int \int \frac{\hat{n}(1)\hat{n}(2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2 \right\} | \Psi_N \rangle$$

$$n^{(2)}(1,2) = \langle \Psi_N | \hat{n}(1)\hat{n}(2) | \Psi_N \rangle = n(1)n(2) + n(1)n_{xc}^{(2)}(1,2)$$

$$E_H[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$E_{xc}[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r}_1) n_{xc}^{\text{hole}}(\mathbf{r}_1, \mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2$$

$$n_{xc}^{\text{hole}}(2|1) = \frac{n_{xc}^{(2)}(1,2)}{n(1)}$$

two-particle correlation function:

$$g(1,2) = \frac{1}{n(1)n(2)} \langle \Psi_N | \hat{n}(1)\hat{n}(2) | \Psi_N \rangle$$

homogenous system:

$$n(\mathbf{r}) = n_0$$

$$g(\mathbf{r}_1, \mathbf{r}_2) = g(\mathbf{r}_2 - \mathbf{r}_1)$$

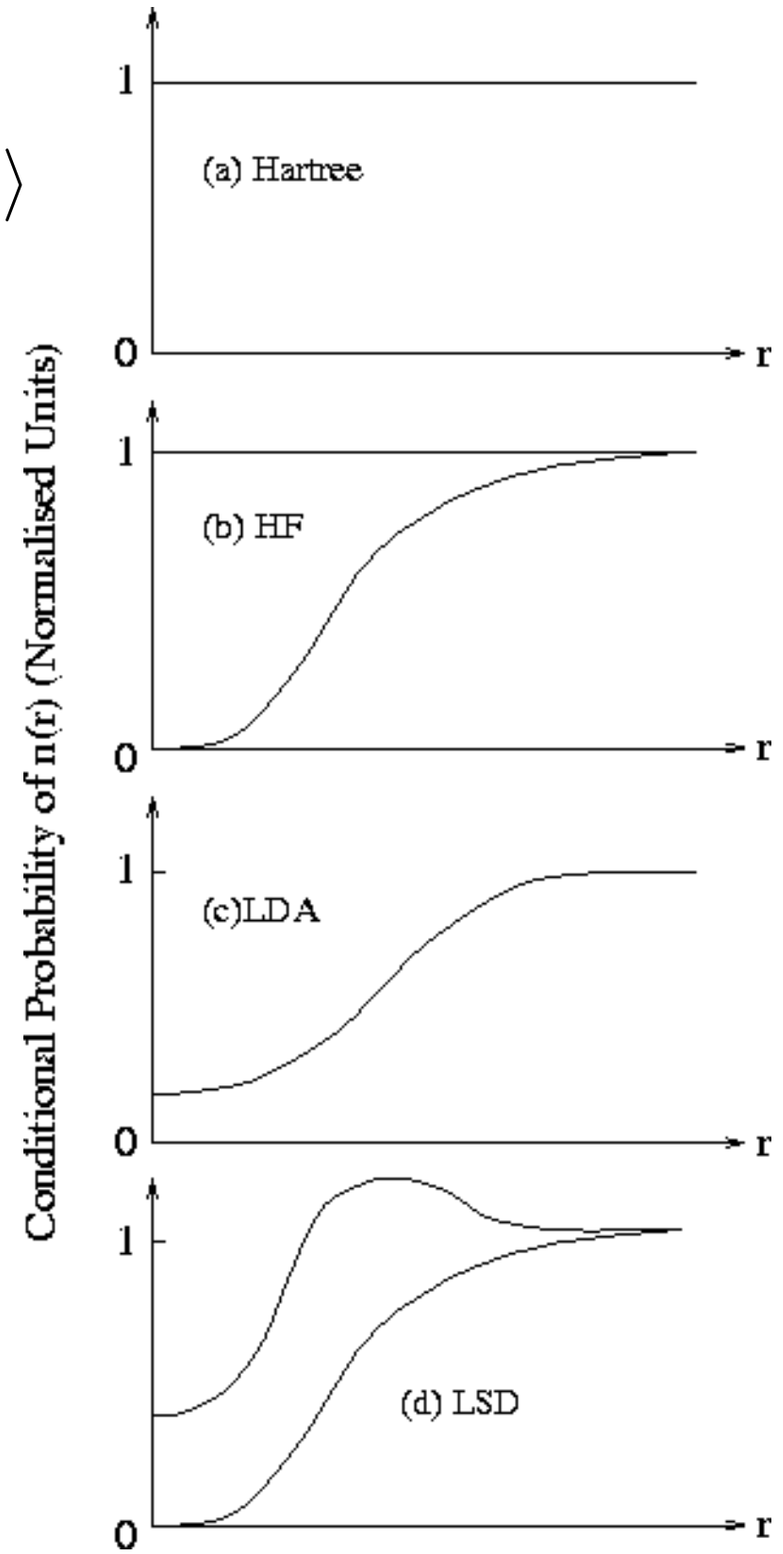
isotropic system:

$$g(r) = g(|\mathbf{r}_2 - \mathbf{r}_1|)$$

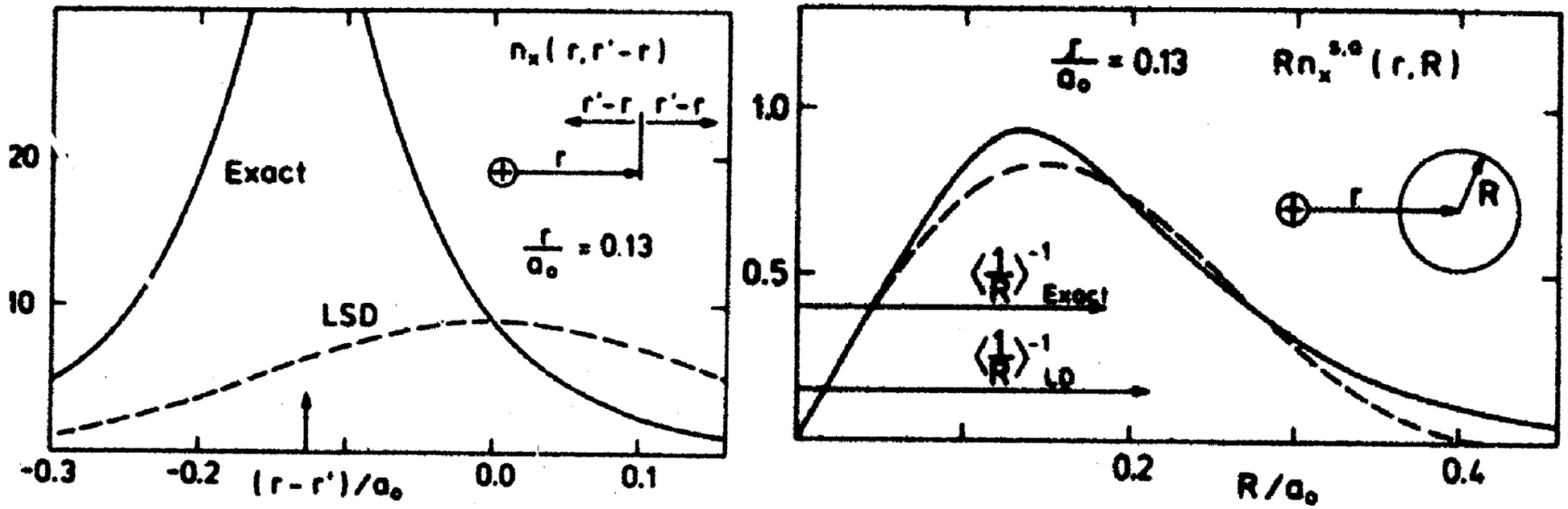
exchange hole:

$$n_{xc}^{\text{hole}}(\mathbf{r}_2|\mathbf{r}_1) = n(\mathbf{r}_2)[g(\mathbf{r}_1, \mathbf{r}_2) - 1]$$

$$\int n_{xc}^{\text{hole}}(\mathbf{r}_2|\mathbf{r}_1) d\mathbf{r}_2 = -1$$

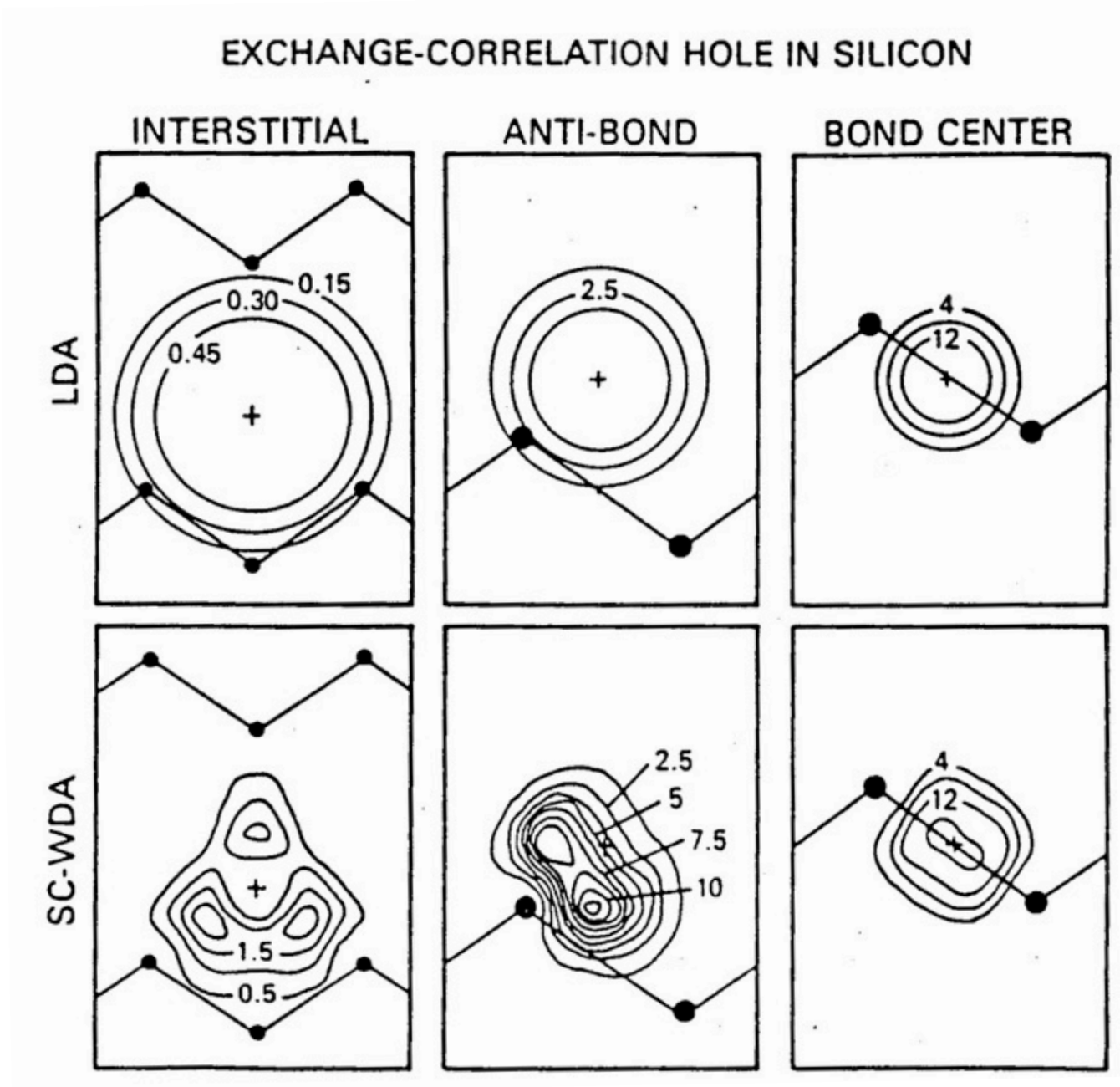


- LDA works well …
  - ✔ Errors in the approximation E_x and E_c cancels each other.
  - ✔ LDA satisfies the sum rule for the exchange-correlation hole:



R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

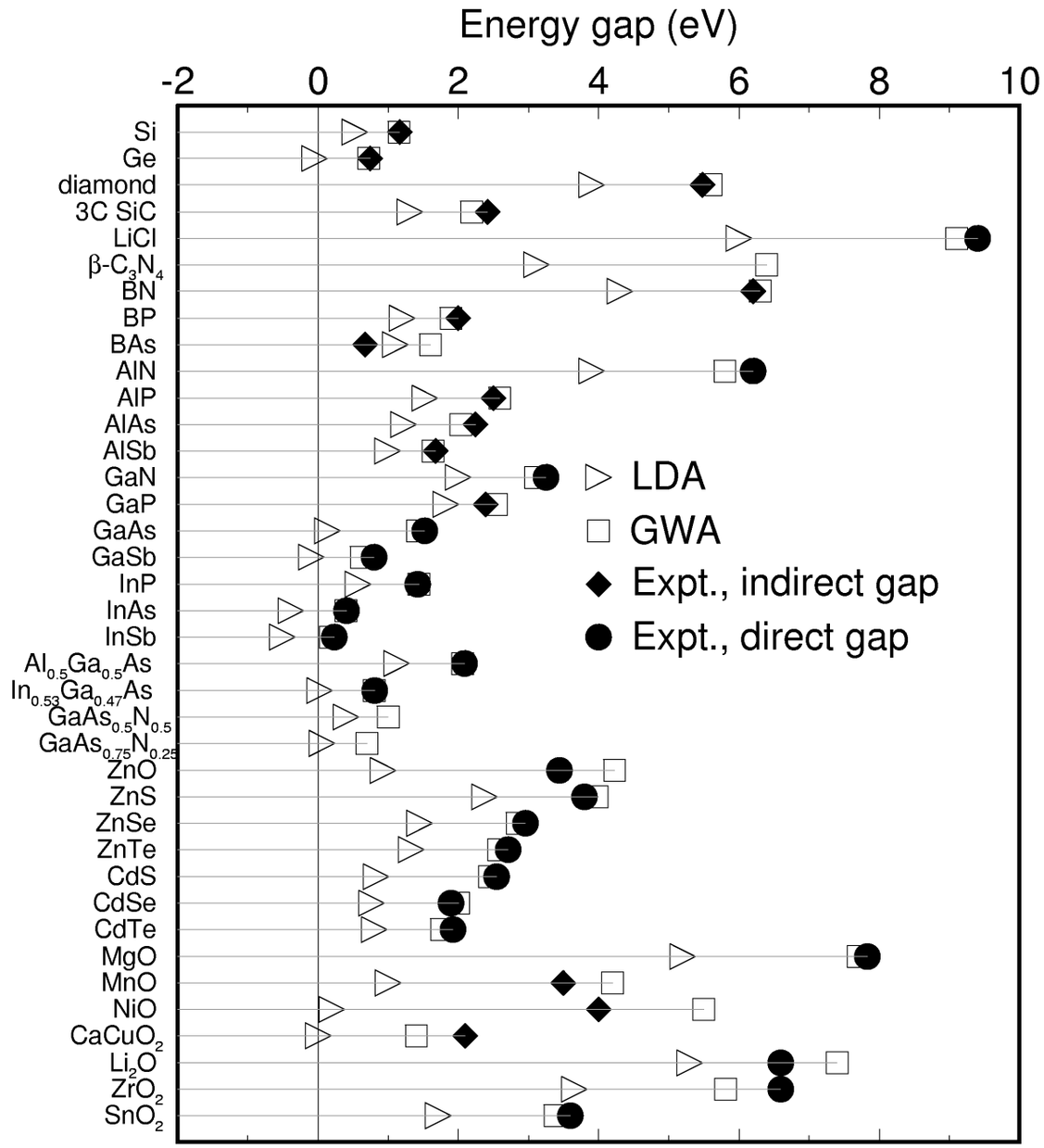
Exchang-correlation holes in Si



When does it works or when does not?

- But, it fails …
  when it deals with the excited state properties

  - ✔ Band-gap problems
  - ✔ Self-interaction problems
  - ✔ Mirror image charges
  - ✔ Two-body correlations
  - ✔ …



The problem is …

- The KS equation deals with a fictitious non-interacting particle, while the excited quasi-particle still experience interactions among particles.

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{eff}}(\mathbf{r}; n_0) + v_{\text{ext}}(\mathbf{r}; \{R_i\})\right] \phi_n(\mathbf{r}) = \varepsilon_n^{\text{KS}} \phi_n(\mathbf{r})$$

- Dyson equation with a self-interaction kernel

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}; \{R_i\})\right] \phi_n(\mathbf{r}) + \sum_{n'} \int d\mathbf{r}' \; \Sigma_{nn'}(\mathbf{r}, \mathbf{r}') \phi_{n'}(\mathbf{r}') = E_n \phi_n(\mathbf{r})$$

- The question is how to describe $\Sigma_{nn'}(\mathbf{r}, \mathbf{r}')$

generalized gradient approximation (GGA)

- It went one step beyond LDA by taking account of the gradient correction, preserving the sum rule.
- a more realistic account of energy barriers and adsorption energies for molecules on metal or semiconductor surfaces

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] = \int d^3r\ n(r)\epsilon_{\mathrm{xc}}(n, \nabla n)$$

- a better description of the exchange hole:

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n] \approx E_{\mathrm{xc}}^{\mathrm{GEA}} = E_{\mathrm{xc}}^{\mathrm{LDA}} + \int d^3r\ C(n)\nabla n/n^{2/3}$$

- But, it is not the way to cure strong interaction problems …

M. Ernzerhof, J. P. Perdew and K. Burke, in Topics in Current Chemistry, 180, (1996).

hybrid functional

Becke's hybrid functional

$$E_{xc} = \alpha E_{xc}^{HF} + (1-\alpha) E_{xc}^{GGA}$$

long range exchange interaction

short range correlation

B3PW91 hybrid functional

$$E_{xc} = E_{xc}^{LSDA} + a_0(E_x^{\text{exact}} - E_x^{LSDA}) + a_x \Delta E_x^{B88} + a_c \Delta E_x^{PW91}$$

- J. P. Perdew, M. Ernzerhof, and K. Burke, J. Chem. Phys. 105, 9982 (1996).
- A. D. Becke, J. Chem. Phys. 98, 5648 (1993).

Outline: Part 2

- Practical DFT calculations
  - total energy calculations
  - Car-Parrinello Method
- Removing “core electrons’’: why and how?
  - pseudo-potentials
- Spin Density Functional Theory
  - self-interaction correction
- Excited states
  - many-body interactions
  - GW approximation
  - single-particle state vs. many-particle state
  - LDA+U
- Prospects:
  - Computational materials physics: a new paradigm

Practical DFT calculations

Total energy calculations

$$
\begin{aligned}
E_{tot} &= \sum_{i=1}^{N} \epsilon_i \\
&\quad -\frac{1}{2}\int\int \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} n(\mathbf{r}_1) n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 \\
&\quad + \int n(\mathbf{r})[\varepsilon_{xc}(n) - v_{xc}(n)] d\mathbf{r} \\
&\quad + E_{ion}
\end{aligned}
$$

KS formalism: $E_v[n(\mathbf{r})] = \int v(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{ion} + T_s[n] + E_H[n] + E_{xc}[n]$

Atomic Simulation Environment

https://wiki.fysik.dtu.dk/ase/

ase.calculators: Energy, force and stress calculators.

```
of hydrogen molecule
>>> from ase import Atoms
>>> from ase.optimize import BFGS
>>> from ase.calculators.nwchem import NWChem
>>> from ase.io import write
>>> h2 = Atoms('H2',
...            positions=[[0, 0, 0],
...                       [0, 0, 0.7]])
>>> h2.calc = NWChem(xc='PBE')
>>> opt = BFGS(h2)
>>> opt.run(fmax=0.02)
BFGS:    0  19:10:49    -31.435229     2.2691
BFGS:    1  19:10:50    -31.490773     0.3740
BFGS:    2  19:10:50    -31.492791     0.0630
BFGS:    3  19:10:51    -31.492848     0.0023
>>> write('H2.xyz', h2)
>>> h2.get_potential_energy()
-31.492847800329216
```

Supported `Calculators`

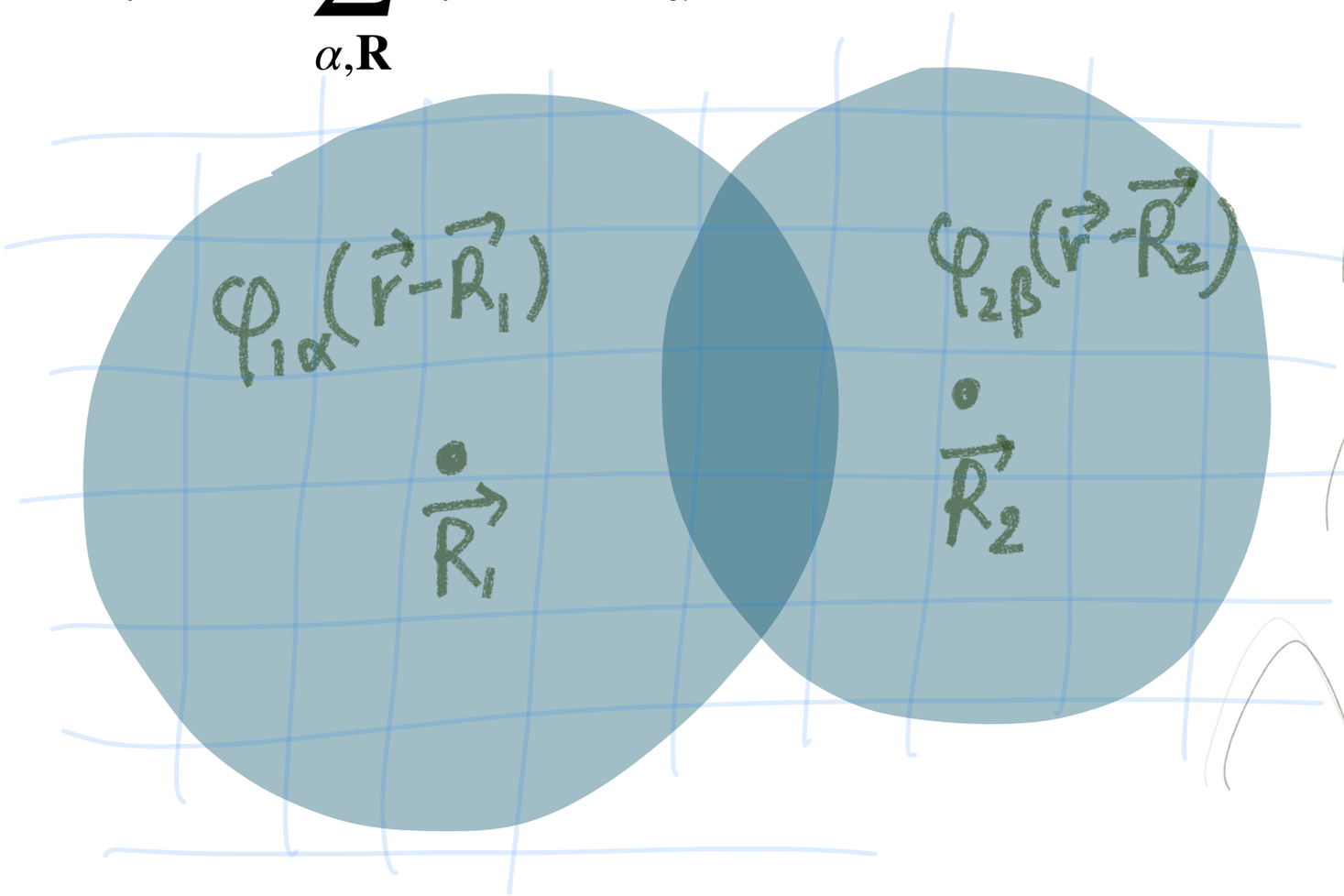
ACE-Molecule amber DMol³ Gaussian Grimme DFT-D3 gulp Mopac qmmm tip3p

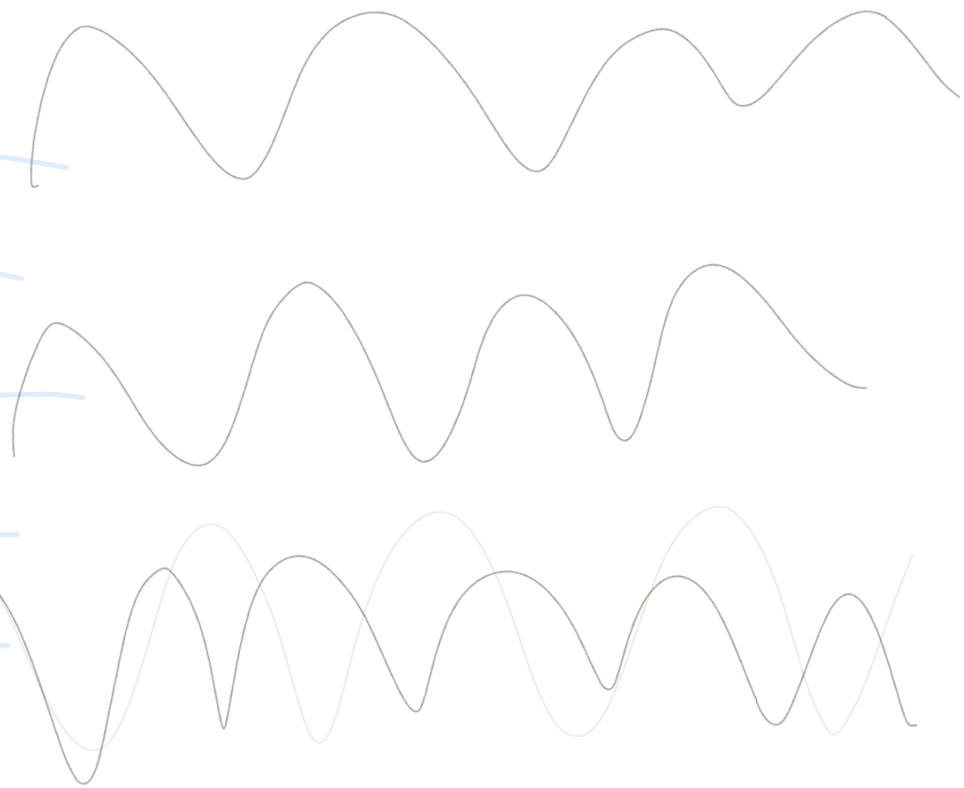
~deMon-Nano

Choice of basis functions

atomic orbital basis, …,

$$\phi_i(\mathbf{r}) = \sum_{\alpha,\mathbf{R}} c_i(\alpha,\mathbf{R})\varphi_\alpha(\mathbf{r}-\mathbf{R})$$





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

plane wave basis … real-space grid

Car-Parrinello Method

Lagrangian Formulation and Ionic Forces

$$\mathcal{L} = \mu \sum_i \int d\mathbf{r} |\dot{\phi}_i(\mathbf{r})|^2 + \frac{1}{2} \sum_I M_I \dot{\mathbf{R}}_I^2 - E_{tot}(\{\phi_i, \mathbf{R}_I\})$$

subject to a set of constraints

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

Equations of motion:

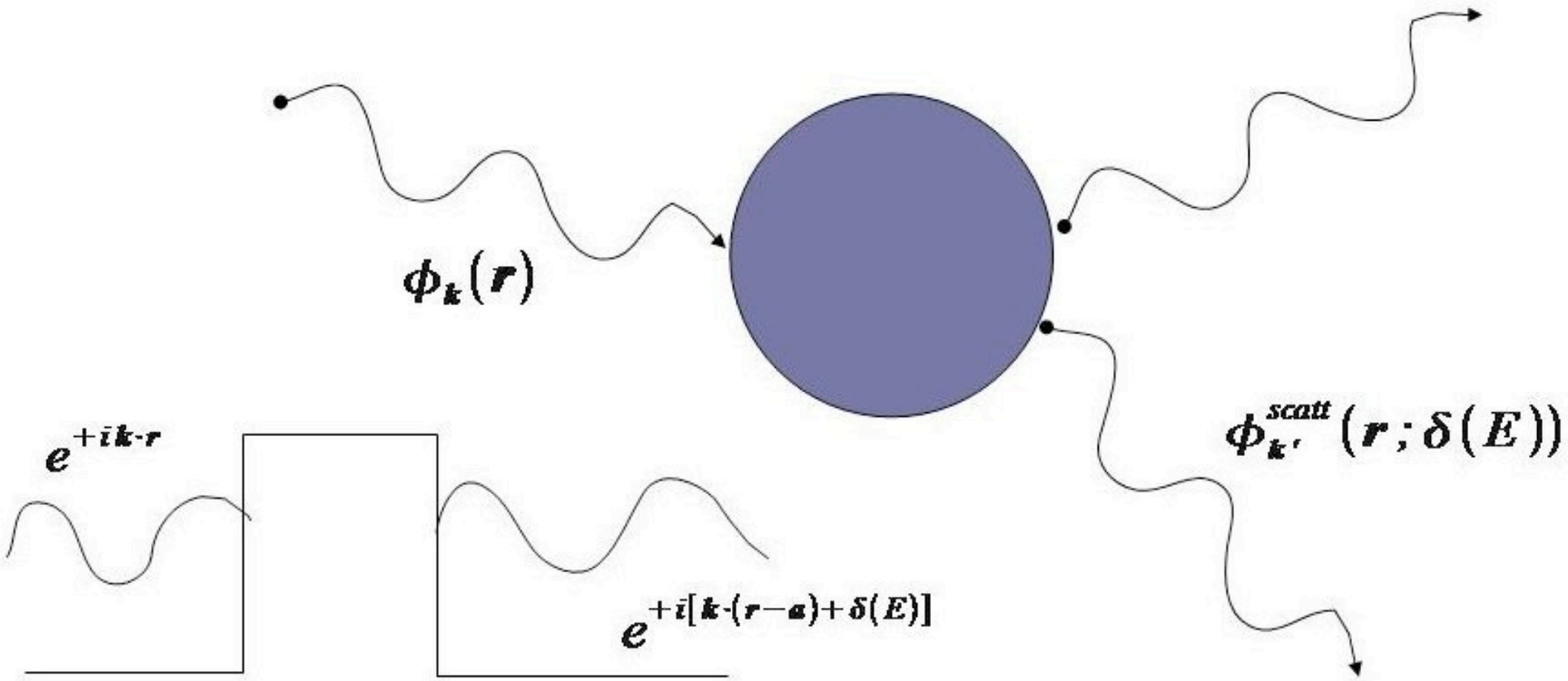
$$\mu \ddot{\phi}_i = -\frac{\delta E_{tot}}{\delta \phi_i^*} + \sum_j \Lambda_{ij} \phi_j$$

$$\mathbf{F}_I = M_I \ddot{\mathbf{R}}_I = -\frac{\partial E_{tot}}{\partial \mathbf{R}_I}$$

Removing “core electrons’’: why and how?

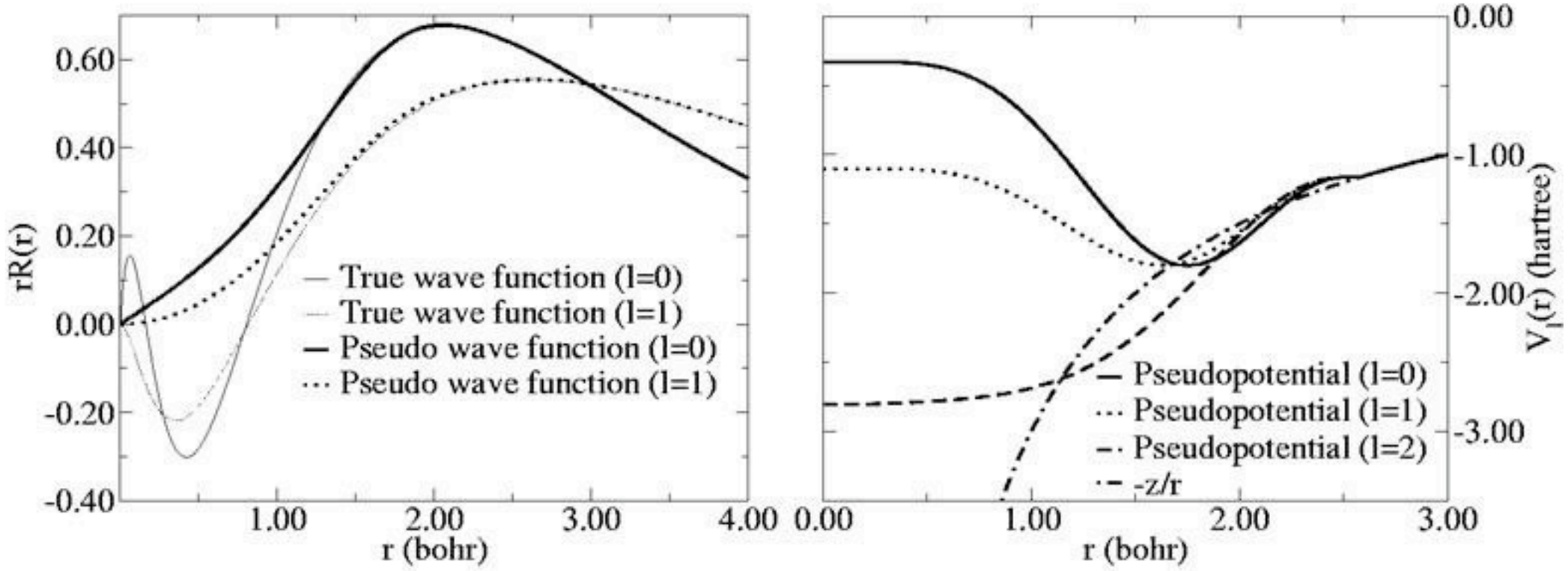
pseudo-potentials

- Interactions between valence electrons and core states can be replaced by a “pseudo-potential”, which provides exactly the same scattering properties mimicking the role of core states.

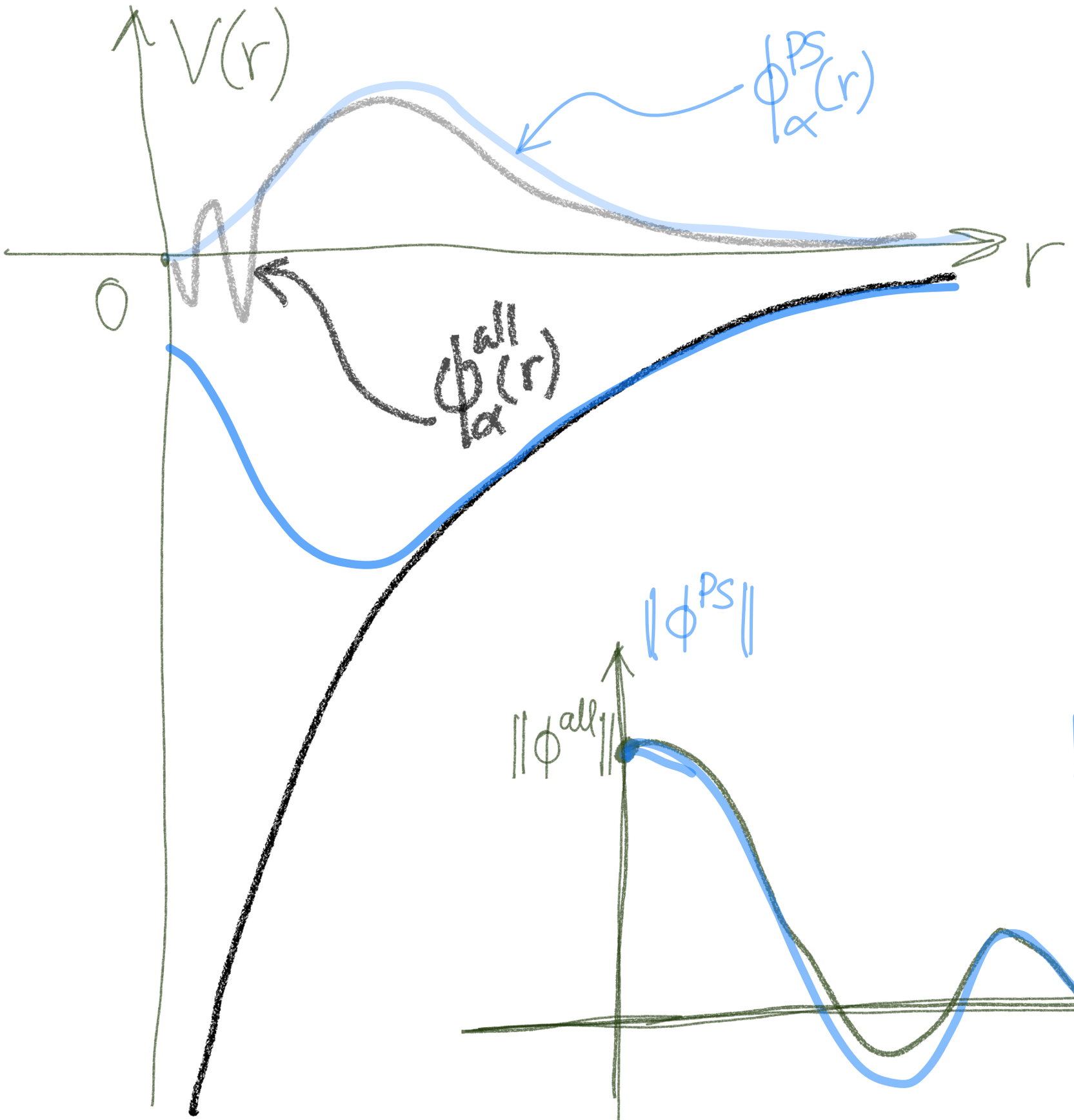


pseudo-potential: matching the boundary conditions …

- Pseudo-potential for Al



$$\frac{d}{dr}\ln\left[rR_{nl}^{AE}(r)\right]_{r=r_c-0}=\frac{d}{dr}\ln\left[r\,\bar{R}_{nl}(r)\right]_{r=r_c+0}$$


V(r)
r
0
$\phi^{PS}_{\alpha}(r)$
$\phi^{all}_{\alpha}(r)$

$\|\phi^{PS}\|$
$\|\phi^{all}\|$
$|\vec{G}_c|$
$|G_c|$
$|G|$

Spin Density Functional Theory

spin-Density Functional Theory

In the presence of $\mathbf{B}(\mathbf{r})$, the basic variables become

$$\{n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r})\}$$

$$n(\mathbf{r}) = \langle\Psi_o|\left(\hat{n}_\uparrow(\mathbf{r}) + \hat{n}_\downarrow(\mathbf{r})\right)|\Psi_o\rangle$$

$$\mathbf{m}_z(\mathbf{r}) = \langle\Psi_o|\left(\hat{n}_\uparrow(\mathbf{r}) - \hat{n}_\downarrow(\mathbf{r})\right)|\Psi_o\rangle$$

Spin Density Functional $E_v[n_\uparrow, n_\downarrow]$:

$$E_v[n_\uparrow, n_\downarrow] = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + \int \mathbf{b}(\mathbf{r})\cdot\mathbf{m}(\mathbf{r})d\mathbf{r}$$
$$+T_s[n_\uparrow, n_\downarrow] + E_H[n] + E_{xc}[n_\uparrow, n_\downarrow]$$

Local Spin-Density Approximation

LSD Exchange Energy Functional:

$$\begin{aligned} E_x^{LSD}[n_\uparrow, n_\downarrow] &= 2^{1/3} C_x \int \left[(n_\uparrow)^{4/3} + (n_\downarrow)^{4/3} \right] d\mathbf{r} \\ &= \frac{1}{2} C_x \int n^{4/3} \left[(1+\zeta)^{4/3} + (1-\zeta)^{4/3} \right] d\mathbf{r} \\ &= \int n \varepsilon_x(n, \zeta) d\mathbf{r} \end{aligned}$$

$$\zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}$$

$$\varepsilon_x(n, \zeta) = \varepsilon_x^o(n) + [\varepsilon_x^1(n) - \varepsilon_x^o(n)] f(\zeta)$$

$$f(\zeta) = \frac{1}{2}(2^{1/3} - 1)^{-1} [(1+\zeta)^{4/3} + (1-\zeta)^{4/3} - 2]$$

self-interaction correction

For $N = 1$ system with $n = n_\sigma(\mathbf{r})$ with $\sigma = \uparrow$ or $\downarrow$, the Coulomb and exchange energy must cancel each other:

$$E_H[n_\uparrow] + E_x[n_\uparrow, 0] = 0$$

$$E_c[n_\uparrow, 0] = 0$$

To eliminate self-interaction in an approximate $\bar{E}_{xc}$,

$$E_{xc}^{SIC}[n_\uparrow, n_\downarrow] = \bar{E}_{xc}[n_\uparrow, n_\downarrow] - \sum_{i\sigma} \left(E_H[n_{i\sigma}] + E_x[n_{i\sigma}, 0]\right)$$

Excited states

Excitation Properties

- Janak's theorem: meaning of $\epsilon_{n\mathbf{k}\sigma}$

  (corresponding to the Koopman's theorem in HF)

$$\frac{\partial E}{\partial n_{i\sigma}} = \epsilon_{i\sigma}$$

- Ionization Energy vs. Electron Affinity:

Excitation energy: $\Delta E = A - I$ for $S + S \rightarrow S^+ + S^-$

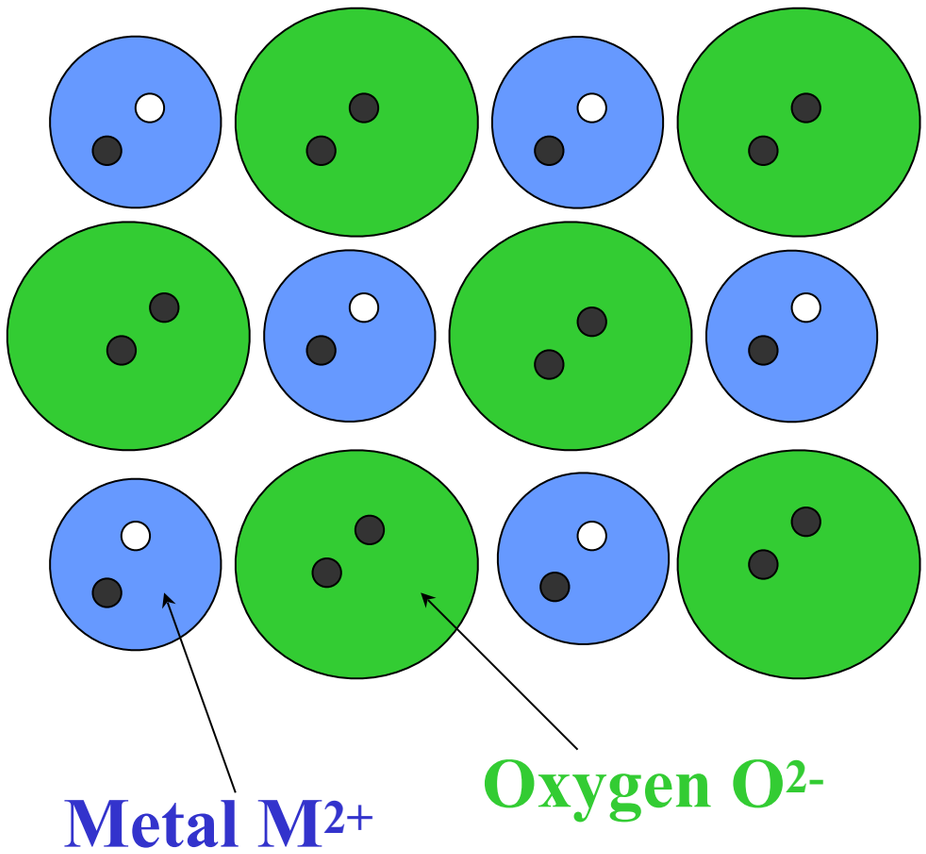
$$I = E(N) - E(N-1)$$

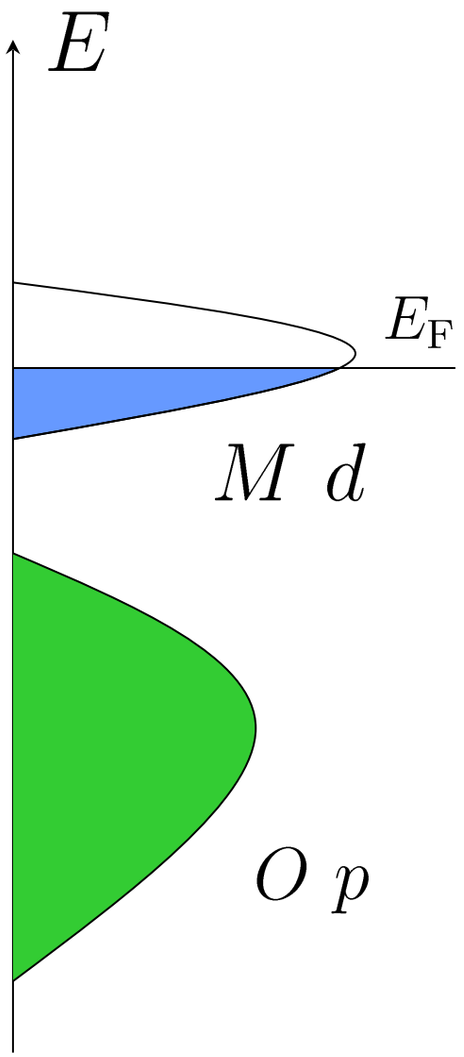
$$A = E(N+1) - E(N)$$

$$\Delta E = E(N+1) + E(N-1) - 2E(N)$$

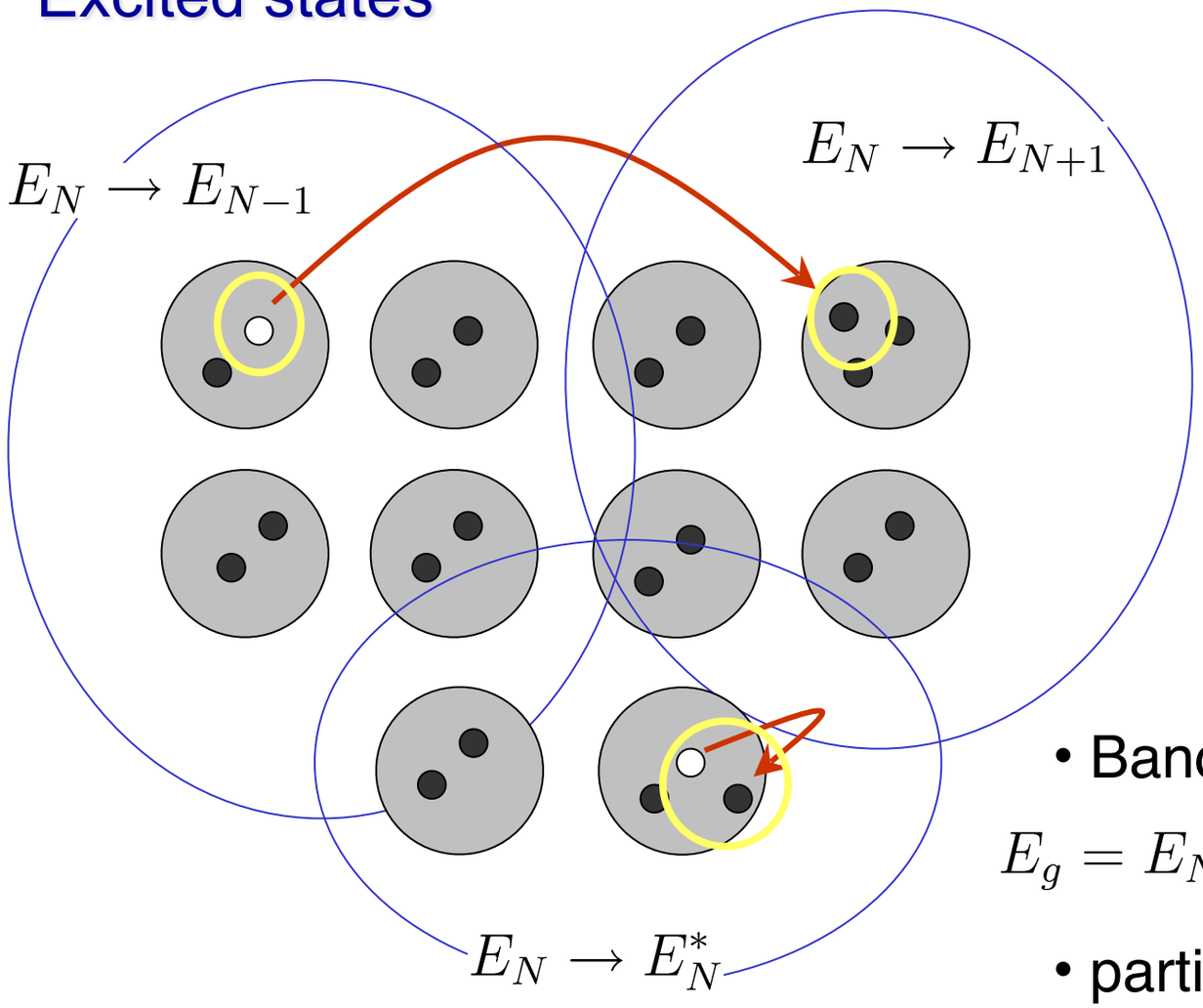
many-body interactions

Transition Metal Oxides





Excited states



- Band gap excitation:

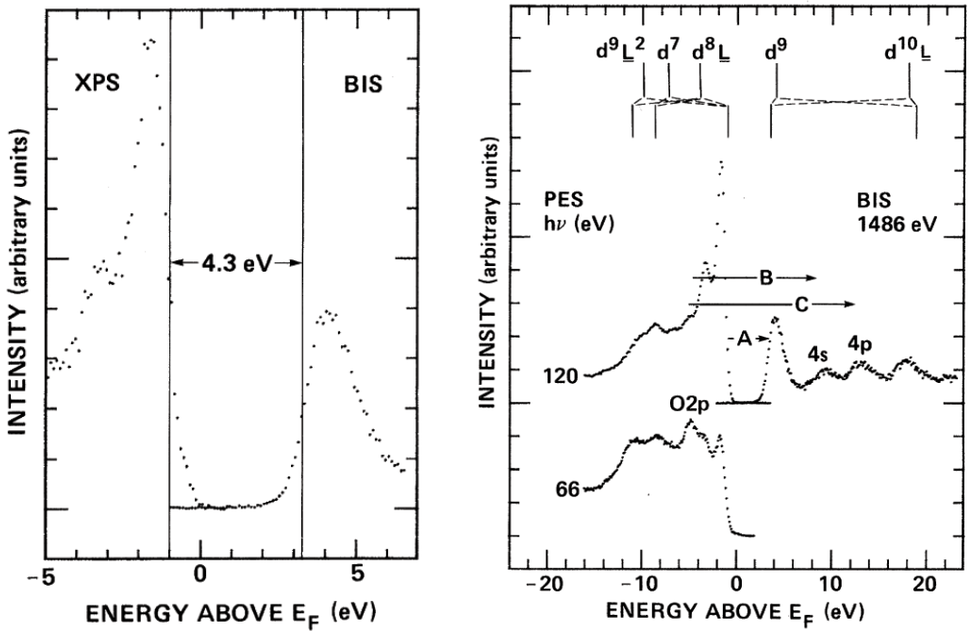
$$E_g = E_{N+1} + E_{N-1} - 2E_N$$

- particle-hole excitation:

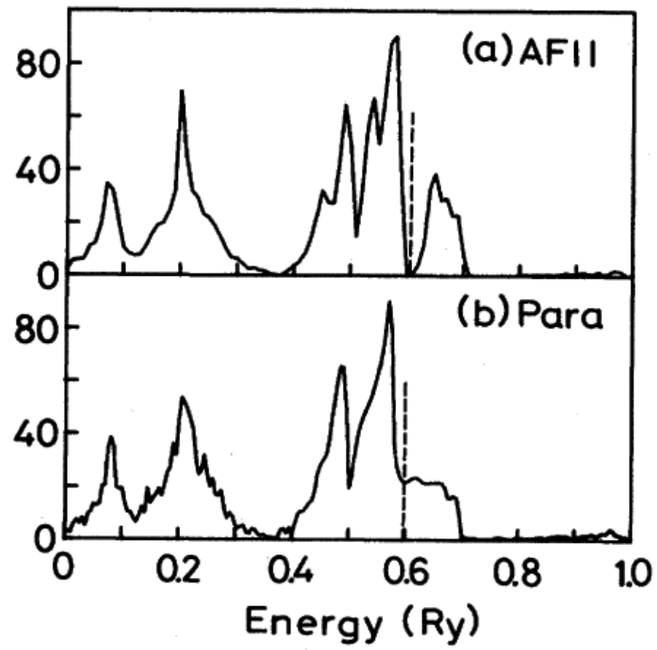
$$E_{\text{ex}} = E_N^* - E_N$$

Transition metal oxides

- an example of strongly correlated electron systems
- NiO: Photoemission spectra vs. LDA predictions



Sawatzky and Allen, Phys. Rev. Lett. (1984)

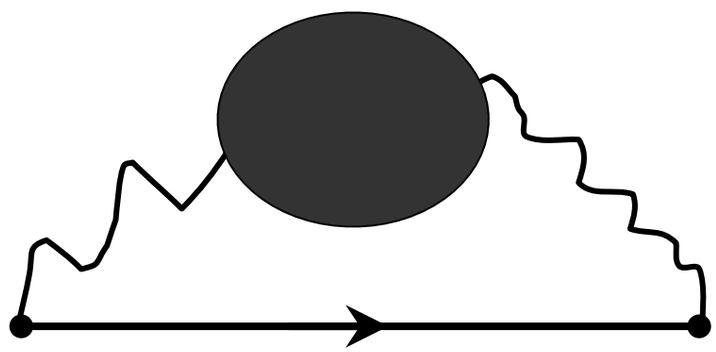


Oguchi *et al.*, Phys. Rev. B (1983)

GW approximation

• Self-energy approximated by

$$\Sigma(\mathbf{r},\mathbf{r}';\omega) \approx$$



$$\Sigma(\mathbf{r},\mathbf{r}';\omega) \approx G(\mathbf{r},\mathbf{r}';\omega)\epsilon^{-1}(\mathbf{r},\mathbf{r}';\omega)V_C(\mathbf{r},\mathbf{r}')$$

$$\epsilon_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega) = \delta_{\mathbf{G}\mathbf{G}'} - v_c(\mathbf{q}+\mathbf{G})\chi_{\mathbf{G}\mathbf{G}'}(\mathbf{q},\omega)$$

• Plasmon pole approximation: in the limit $\mathbf{q} \to 0$

$$\epsilon(q \to 0,\omega) = 1 - \frac{4\pi n_e^2}{\omega^2}$$

• What is n_e when some of the electrons in the system is *localized*?

time-dependent DFT

$$\Psi_N(\{\mathbf{r}_i\};t) = e^{-i\mathscr{H}t}\Psi_N(\{\mathbf{r}_i\};t=0)$$

$$e^{-i\hat{H}t}|\Psi_N\rangle = \sum_n c_n e^{-iE_n t}|\Phi_{N,n}\rangle$$

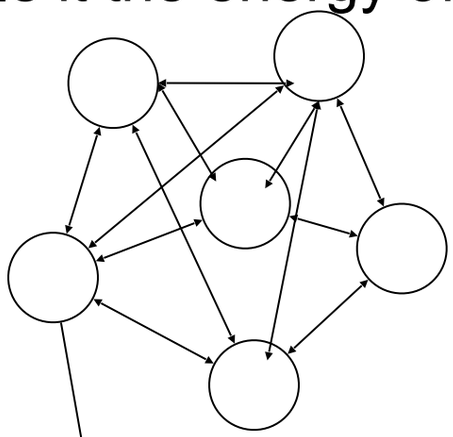
$$\hat{H}|\Phi_{N,n}\rangle = E_n|\Phi_{N,n}\rangle$$

$$|\Psi_N\rangle = \sum_n c_n|\Phi_{N,n}\rangle$$

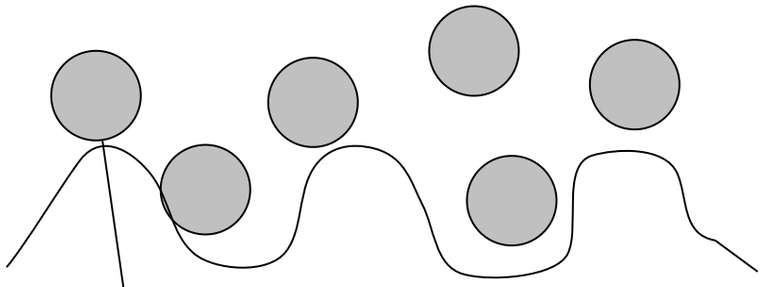
single-particle state vs. many-particle state

Band energy? What do we measure?

- Is it the energy of a real electron which we measure?

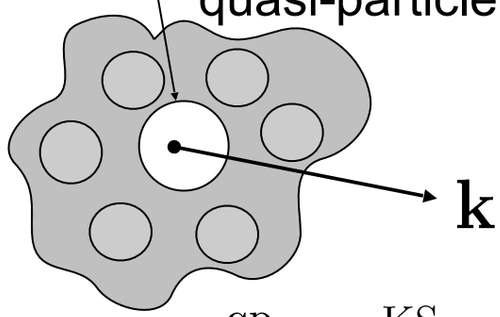


interacting electrons



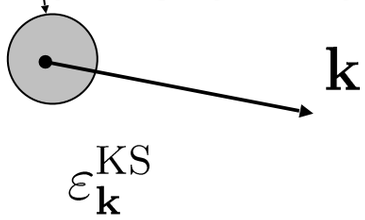
non-interacting electrons
under an effective potential

quasi-particle



$$E_{\mathbf{k}}^{\mathrm{qp}} = \varepsilon_{\mathbf{k}}^{\mathrm{KS}} + \Sigma_{\mathbf{k}}(E_{\mathbf{k}}^{\mathrm{qp}})$$

Kohn-Sham “fictitious” particle



$\varepsilon_{\mathbf{k}}^{\mathrm{KS}}$

LDA+U

- Strong on-site Coulomb interaction as a source of strong electron correlation
- Hubbard model:

$$H = \sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^{+} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

multiplet states

$$|\Psi\rangle = \sum_{\{n_\alpha\}} c_{\{n_\alpha\}} |\Phi\{n_\alpha\}\rangle$$

$$\hat{H}^{\mathrm{KS}} = \sum_{ij} \langle \phi_i | \hat{H} | \phi_j \rangle c_i^{+} c_j$$

$$E_{\mathrm{LDA}}[n_0] = \langle \Psi_0 | \hat{H}_{\mathrm{KS}} | \Psi_0 \rangle$$

A mean field solution

$$\hat{H}_1 = \hat{H} - E_{\mathrm{LDA}}^{\mathrm{KS}}[n_0]$$

A fluctuation term
due to Coulomb interactions

Prospects

Computational materials physics: a new paradigm

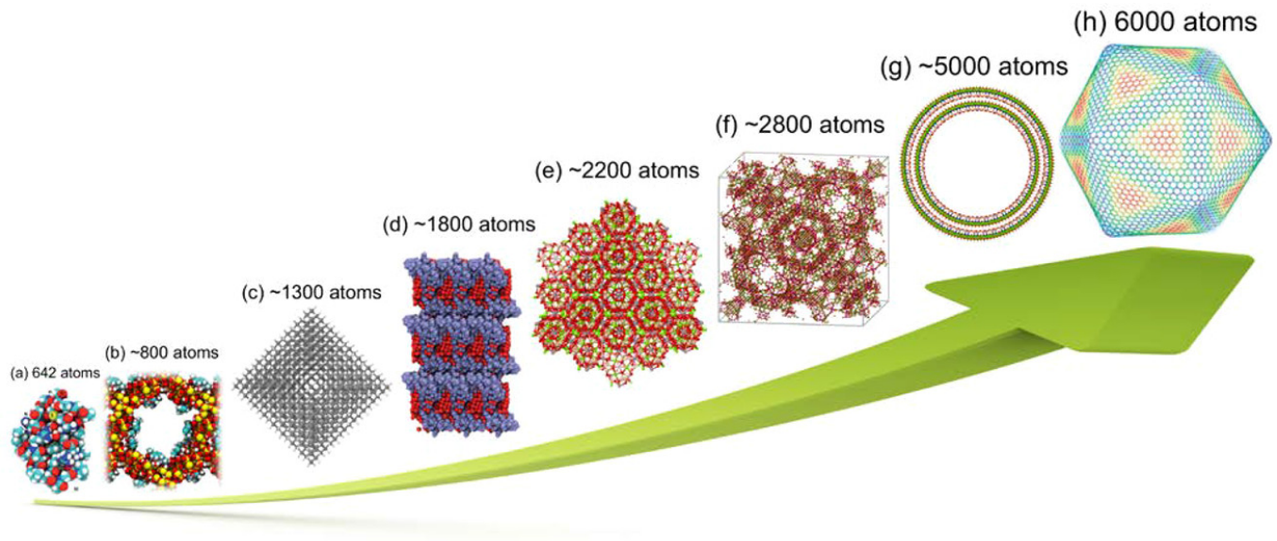
- Density functional theory is one of the most powerful technique in theoretical condensed matter physics
- Major contributions to material science, biological science, …
- Computational materials design:
  - Predictive power for the structure of a new material
  - Various physical properties
  - Crystal phase transitions in bulk or at surfaces
  - Surfaces structure, chemical reactions, catalysis, thermal desorption
  - Excited states, core-level spectroscopy (many-body effects), photo- chemistry, etc.
  - Crystal growth and self-organization of nano-scale structures

Why machine-learning methods?

Large-Scale Condensed Matter DFT (Density Functional Theory) Simulations

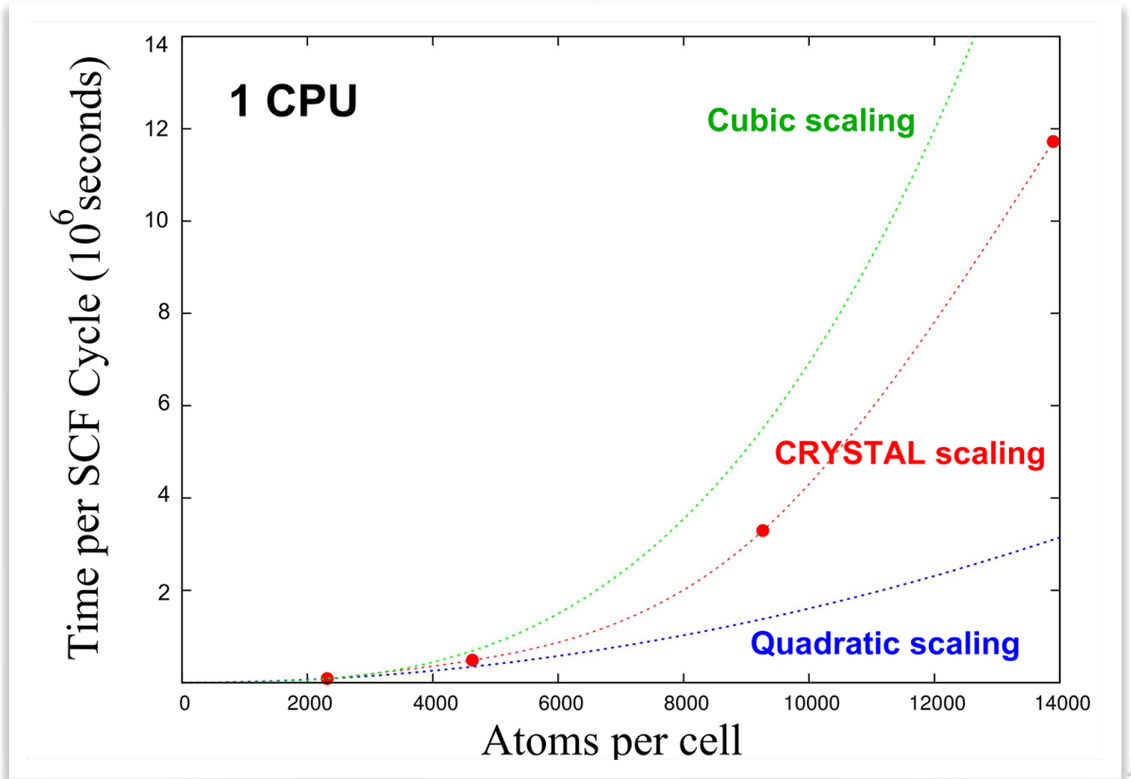
Still expensive calculations!

- Computational cost:
  $\sim o(N_e^3)$ or $o(N_e^2)$ at best
- self-consistency issue:
  ~ small gap materials
- difficult to describe
  time-evolution
  when energy barriers
  are present
- and many other issues …



Solving Kohn-Sham equations ~ o(N^3)

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\boldsymbol{r}) + v_H(\boldsymbol{r}) + v_{xc}(\boldsymbol{r})\right)\psi_i(\boldsymbol{r}) = \epsilon_i\psi_i(\boldsymbol{r})$$



A. Erba et al., J. Chem. Theory Comput. (2017)

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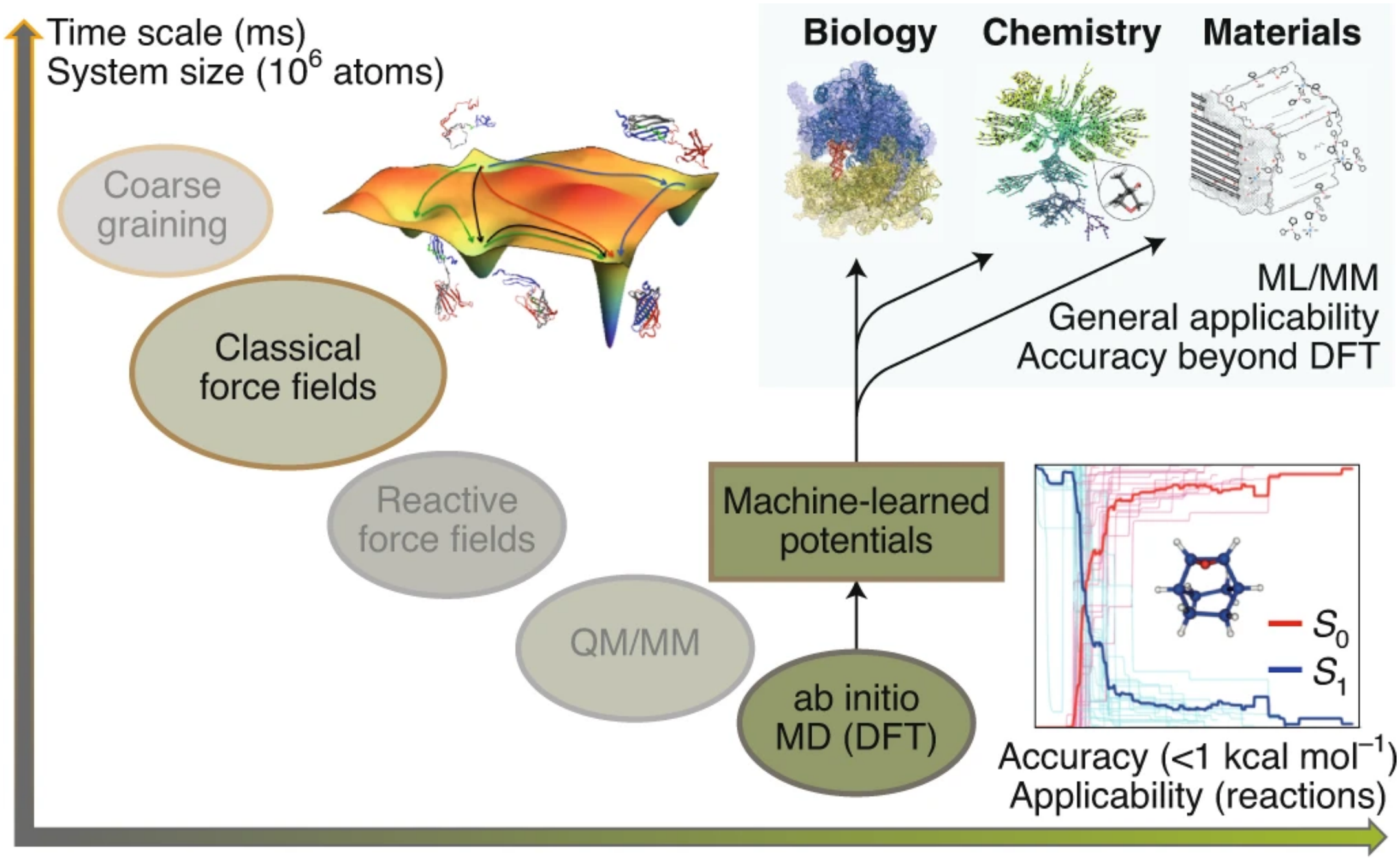

Friederich, P., Häse, F., Proppe, J. et al.,Nat. Mater. 20, 750–761 (2021).