

Density Functional Theory based Molecular Dynamics Tutorial

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tutorial CPMD-CP2K

"We present a unified scheme that, by combining molecular dynamics and density-functional theory, profoundly extends the range of both concepts."

R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471-2474 (1985).

Program I

Tuesday

lecture 1 : Overview of Density Functional theory (RV)

lecture 2 : DFT in plane wave basis sets : implementation (FXC)

Wednesday

lecture 3 : Optimization techniques (MS)

lecture 4 : DFT in gaussian basis sets : implementation (RV)

Program II

Thursday

lecture 5 : Ab initio molecular dynamics techniques (MS)

lecture 6 : Wannier functions (CS)

Friday

lecture 7 : Property calculations (RV)

lecture 8 : Free energy calculations (FXC)

Overview of Density Functional Theory

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Born-Oppenheimer approximation

Total Hamiltonian of the system atoms+electrons

$$\hat{H}_T = \hat{T}_N + \hat{V}_{NN} + \hat{H}$$

$M_I \gg m_e \rightarrow$ approximate system wavefunction

$$\Psi_S(\vec{R}_I, \vec{r}_1, \dots, \vec{r}_N) = \Psi(\vec{R}_I) \Psi_0(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_I)$$

$\Psi_0(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_I)$: the ground state electronic wavefunction of the electronic Hamiltonian \hat{H} at fixed ionic configuration $\{\vec{R}_I\}$

ionic Hamiltonian for the evolution of the nuclei wavefunction

$$\hat{H}_N = \hat{T}_N + \hat{V}_{NN} + E_0(\hat{\vec{R}}_I)$$

Energy of the electrons at this ionic configuration

$$E_0(\vec{R}_I) = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle$$

Classical limit for the nuclei

The potential energy surface for the nuclei motion is
 $v_{NN}(\vec{R}_I) + E_0(\hat{\vec{R}}_I)$

Born-Oppenheimer Molecular Dynamics

1. from the ionic configuration $\mathbf{R}(t)$ at time t compute the total energy $E_0 = E_0[\mathbf{R}(t)]$ given a representation of the electronic state :

$$\Psi_0(\vec{r}_1, \dots, \vec{r}_N; \vec{R}_I(t))$$

2. we then get the forces from the Hellman-Feynman theorem

$$F_I(t) = -\frac{\partial E_0}{\partial R_I} = -\left. \frac{\partial E}{\partial R_I} \right|_{\phi_i = \phi_i^0} = \int d^3\vec{r} \frac{\partial V_{\text{ext}}(\vec{r}, \mathbf{R}(t))}{\partial R_I}$$

3. advance ionic configuration $\mathbf{R}(t) \rightarrow \mathbf{R}(t + \delta t)$ by solving Newton's equations of motion (Verlet algorithm)
4. back to step 1

The total energy $\frac{1}{2} \sum_I M_I \dot{R}_I^2(t) + E_0(t)$ is in principle conserved

Interacting electrons

Hamiltonian (in atomic units) for an N electrons system

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}_{ext}$$

kinetic energy operator

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \hat{\nabla}_i^2$$

electron-electron repulsion

$$\hat{V}_{ee} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\hat{\vec{r}}_i - \hat{\vec{r}}_j|}$$

where $\hat{\vec{r}}_i$ is the position operator for electron i

Ground state wavefunction

$\Psi_0(\vec{r}_1, \dots, \vec{r}_N)$ function of $3N$ variables

satisfies (fermions)

$$\Psi_0(\vec{r}_1, \dots, \vec{r}_i, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N) = -\Psi_0(\vec{r}_1, \dots, \vec{r}_j, \dots, \vec{r}_i, \dots, \vec{r}_N)$$

We have

$$\hat{H}\Psi_0(\vec{r}_1, \dots, \vec{r}_N) = E_0\Psi_0(\vec{r}_1, \dots, \vec{r}_N)$$

or, alternatively, Ψ_0 can be obtained from a variational principle :

$$E_0 = \min_{\Psi(\vec{r}_1, \dots, \vec{r}_N)} \langle \Psi | \hat{H} | \Psi \rangle.$$

The minimization of $\langle \Psi | \hat{H} | \Psi \rangle$ is realized for $\Psi = \Psi_0$ (non-degenerate ground state).

Reminder : Hartree-Fock approximation

Wavefunction ansatz

$$\Psi^{HF}(\vec{r}_1, \dots, \vec{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\vec{r}_1) & \phi_2(\vec{r}_1) & \dots & \phi_N(\vec{r}_1) \\ \vdots & & & \vdots \\ \phi_1(\vec{r}_N) & \dots & \dots & \phi_N(\vec{r}_N) \end{vmatrix}$$

single Slater determinant (ϕ_i single electron orbitals)

Ψ_0^{HF} obtained by minimization of $\langle \Psi^{HF} | \hat{H} | \Psi^{HF} \rangle$

However Ψ_0 is not in general a single determinant except for non-interacting particles (correlation effects)

Outline of Density Functional Theory

Instead of using the full electronic wavefunction $\Psi_0(\vec{r}_1, \dots, \vec{r}_N)$, the electronic **ground state** of a system can be entirely described by

- ▶ its electron density $n(\vec{r})$ (Hohenberg-Kohn theorem)
- ▶ or, alternatively, by N one-electron orbitals $\phi_1(\vec{r}), \dots, \phi_N(\vec{r})$ giving rise to the same density $n(\vec{r})$:

$$N \int \cdots \int d^3\vec{r}_2 \dots d^3\vec{r}_N |\Psi(\vec{r}, \dots, \vec{r}_N)|^2 = n(\vec{r}) = \sum_{i=1}^N |\phi_i(\vec{r})|^2$$

(Kohn-Sham theorem)

$n(\vec{r})$ or $\phi_1(\vec{r}), \dots, \phi_N(\vec{r})$ are obtained by **minimization** of a **density functional**

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The Hohenberg-Kohn theorem

Existence of a map $n(\vec{r}) \rightarrow v(\vec{r})$

$$\begin{array}{c} v(\vec{r}) \rightarrow \Psi_0 \rightarrow n(\vec{r}) \\ \longleftarrow \text{HK theorem} \end{array}$$

Knowledge of $n(\vec{r})$ gives knowledge of $v(\vec{r})$ and of Ψ_0 ,

thus all properties of the electronic system and in particular any expectation value of an observable $\hat{O} = \langle \Psi | \hat{O} | \Psi \rangle$, are functionals of $n(\vec{r})$ ($O[n]$ for the observable \hat{O}).

Lemma

Defining the set \mathcal{V} of external potentials $v_{\text{ext}}(\vec{r})$ leading to a **non-degenerate** ground state

and

$\{\Psi\}$ the set of wavefunctions $\Psi(\vec{r}_1, \dots, \vec{r}_N)$ which **are ground state wavefunctions** of a system of N electron in an external potential,

the application : $\mathcal{V} \mapsto \{\Psi\}$ is bijective.
 $v_{\text{ext}} \rightarrow \Psi_0$

- surjectivity : by definition

- injectivity :

Provided that $v_{ext} - v'_{ext} \neq cte$, v_{ext} and v'_{ext} can not have the same ground state.

If there was such a common ground state Ψ , it would verify :

$$\begin{aligned}(\hat{T} + \hat{V}_{ee} + \hat{V}_{ext}) \Psi &= E_0 \Psi \\(\hat{T} + \hat{V}_{ee} + \hat{V}'_{ext}) \Psi &= E'_0 \Psi,\end{aligned}$$

leading to $(\hat{V}_{ext} - \hat{V}'_{ext})\Psi = (E_0 - E'_0)\Psi$,

that is $v_{ext} - v'_{ext} = E_0 - E'_0$ if Ψ is not identically zero,

in contradiction with the above assumption.

The HK theorem

Let's now define the set \mathcal{N} of ground state electron densities

the application : $\{\Psi\} \mapsto \mathcal{N}$ is bijective.
 $\Psi_0 \rightarrow n(\vec{r})$

- surjectivity : by definition
- injectivity :

let's assume that Ψ and Ψ' , ground states of the potentials v and v' ($v - v' \neq cte$) lead both to the same electron density $n(\vec{r})$

denoting $\hat{H} = \hat{T} + \hat{V}_{ee} + \hat{V}$ and $\hat{H}' = \hat{T} + \hat{V}_{ee} + \hat{V}'$, we have :

$$\begin{aligned}\langle \Psi | \hat{H} | \Psi \rangle &< \langle \Psi' | \hat{H} | \Psi' \rangle \\ E_0 &< \langle \Psi' | \hat{H}' | \Psi' \rangle + \langle \Psi' | (\hat{V} - \hat{V}') | \Psi' \rangle \\ E_0 &< E'_0 + \int d^3\vec{r} n(\vec{r}) (v(\vec{r}) - v'(\vec{r}))\end{aligned}$$

and similarly

$$E'_0 < E_0 + \int d^3\vec{r} n(\vec{r}) (v'(\vec{r}) - v(\vec{r}))$$

When the two inequalities are added, one is lead to an obvious contradiction :

$$E_0 + E'_0 < E_0 + E'_0$$

Energy functional

The total energy of the system is now a **functional** $E[n]$ of the density. We can write it as

$$E[n] = \int d^3\vec{r} n(\vec{r})v(\vec{r}) + F_{HK}[n]$$

with

$$F_{HK}[n] = T[n] + V_{ee}[n] \quad (1)$$

$$T[n] = \langle \Psi[n] | \hat{T} | \Psi[n] \rangle \quad (2)$$

$$V_{ee}[n] = \langle \Psi[n] | \hat{V}_{ee} | \Psi[n] \rangle \quad (3)$$

F_{HK} is **universal** (defined only for v -representable densities)

Variational principle

For a given external potential $v_0(\vec{r})$, we define an energy functional $E_{v_0}[n]$ as

$$E_{v_0}[n] = \int d^3\vec{r} n(\vec{r})v_0(\vec{r}) + F_{HK}[n]$$

then $E_{v_0}[n]$ is minimal for $n = n_0$, the ground state density of v_0 :

$$E_0 = E[n_0] < F_{HK}[n] + \int d^3\vec{r} n(\vec{r})v_0(\vec{r}) \text{ for } n(\vec{r}) \neq n_0(\vec{r})$$

Demo of the variational principle

for $n(\vec{r}) \neq n_0(\vec{r})$

$$E_{v_0}[n] = \langle \Psi[n] | \hat{T} + \hat{V}_{ee} + \hat{V}_0 | \Psi[n] \rangle$$

$\Psi[n]$ is not ground state of v_0 so

$$\langle \Psi[n] | \hat{T} + \hat{V}_{ee} + \hat{V}_0 | \Psi[n] \rangle > \langle \Psi[n_0] | \hat{T} + \hat{V}_{ee} + \hat{V}_0 | \Psi[n_0] \rangle = E[n_0]$$

Some remarks about the F_{HK} functional

- ▶ Unfortunately F_{HK} is not known and one has to make approximations for it.
- ▶ It can be shown that $F_{HK}[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle$, realised for $\Psi = \Psi[n]$

The Thomas-Fermi Functional

$$F_{HK}[n] = \int d^3\vec{r} C_F n(\vec{r})^{\frac{5}{3}} + \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

- ▶ $C_F n(\vec{r})^{\frac{5}{3}}$: Kinetic energy of a uniform electron gas of independent electrons with density $\bar{n} = n(\vec{r})$
- ▶ $J[n] = \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|}$: Hartree “Mean-field” term

$$C_F = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} \approx 2.8712$$

Minimization of the TF functional

For a given v_0 we want to minimize

$$E_{v_0} = \int d^3\vec{r} C_F n(\vec{r})^{\frac{5}{3}} + \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d^3\vec{r} n(\vec{r})v_0(\vec{r})$$

with the constraint $\int d^3\vec{r} n(\vec{r}) = N$

To do so, we use a Lagrange multiplier μ (chemical potential) and we minimize instead

$$E_{v_0} - \mu \left(\int d^3\vec{r} n(\vec{r}) - N \right)$$

Derivating with respect to $n(\vec{r})$, the condition for $n(\vec{r})$ to be an extremum reads now

$$\frac{5}{3} C_F n(\vec{r})^{\frac{2}{3}} + \int d^3\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_0(\vec{r}) = \mu$$

TF theory for neutral atoms

Let's consider the case of an atom, then

$$v_0(\vec{r}) = -\frac{Z}{r}$$

For a neutral atom, we have $\mu = 0$, then if we call ϕ the electrostatic potential :

$$\frac{5}{3} C_F n(r)^{\frac{2}{3}} = -\phi(r)$$
$$\nabla^2 \phi(r) = n(r)$$

1. $n(r) \rightarrow \alpha \frac{1}{r^6}$ as $r \rightarrow \infty$

2. $E_0 = -c_1 Z^{7/3}$

3. $n_0(r) = Z^2 n_1(Z^{1/3} r)$

c_1 and n_1 are the **exact** limit behaviour as $Z \rightarrow \infty$

E. H. Lieb and B. Simon, Phys. Rev. Lett. **31**, 681 (1973).

E. H. Lieb, Rev. Mod. Phys. **53**, 603 (1981).

Regions of electronic cloud

1. Inner core region of size $\approx Z^{-1/3}$ with density $\approx Z^2$ and $\approx Z$ electrons
2. Mantle core with $n \approx \alpha \frac{1}{r^6}$ (independent of Z) and size also $\approx Z^{-1/3}$
3. A complicated intermediate region
4. Outer shell of size 1 and $\approx Z^{2/3}$ electrons. Chemistry takes place here !
5. Outside region where density decays exponentially.

TF functional

- ▶ leads to densities with wrong asymptotic behavior
- ▶ no bonding
- ▶ however gives reasonable energies for true electronic densities
- ▶ recover correct densities as $Z \rightarrow \infty$

Spinless fermions in a flat box

Particle in a box

$$\epsilon_j = \frac{\pi^2}{2} j^2; \phi_j(x) = \sqrt{2} \sin \pi j x; j = 1, 2, 3, \dots$$

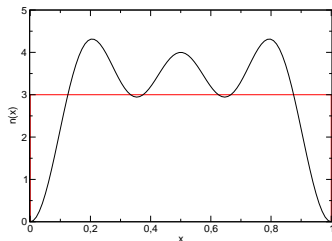
$$E(N) = \sum_{j=1}^N \epsilon_j = \frac{\pi^2}{6} N(N + \frac{1}{2})(N + 1) = T$$

LDA (TF) approximation

$$T^{LDA} = \int dx t(n(x)); t(n) = \frac{\pi^2}{6} n^3$$

$$\Rightarrow n^{LDA}(x) = \text{cte} = N \rightarrow T^{LDA} = \frac{\pi^2}{6} N^3$$

Spinless fermions in a flat box



Exact and LDA densities for 3 fermions in a box

Local Density Approximation to the kinetic energy

- ▶ Approximation for many electron systems
- ▶ Works best for large N
- ▶ Local approximation are crudely correct but miss crucial details for chemistry

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The Kohn-Sham method

Postulate an auxiliary set of one electron orbitals $\{\phi_i\}$ solution of a system of N **non-interacting** electrons, in an external potential v_s ,

$$\begin{aligned}\hat{H}_s \phi_i &= \epsilon_i \phi_i & \langle \phi_i | \phi_j \rangle &= \delta_{ij} \\ \hat{H}_s &= -\frac{1}{2} \nabla^2 + v_s(\vec{r}) & \Psi_s &= \frac{1}{N!} \det[\phi_1 \phi_2 \dots \phi_N]\end{aligned}$$

such as

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

If this is possible $n(\vec{r})$ is said to be non-interacting v -representable

Then from a Hohenberg-Kohn theorem for non-interacting electrons, the map $n(\vec{r}) \Leftrightarrow v_s(\vec{r}) \Leftrightarrow \{\phi_i(\vec{r})\}$ is unique

Total energy decomposition I

The total energy of the system can be decomposed into

$$E[n] = T_s[n] + \int d^3\vec{r} n(\vec{r})v(\vec{r}) + J[n] + E_{xc}[n]$$

with

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

recall that $\phi_i \equiv \phi_i[n]$ and

$$T_s[n] = \min_{\substack{\{\phi_i\} \rightarrow n \\ \langle \phi_i | \phi_j \rangle = \delta_{ij}}} \sum_{i=1}^N \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle$$

(cures the major deficiencies of TF functional)

Total energy decomposition II

$$J[n] = \frac{1}{2} \iint d^3\vec{r} d^3\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} : \text{Hartree term}$$

and finally $E_{xc}[n]$ is the exchange correlation energy :

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

The Kohn-Sham potential

- $n(\vec{r})$ minimizes $E[n]$

let's assume a small variation of n , $\delta n(\vec{r})$, which conserves the number of electrons ($\int d^3\vec{r} \delta n(\vec{r}) = 0$)

$$\delta E = \delta T_s + \int d^3\vec{r} \left(v(\vec{r}) + \frac{\partial J}{\partial n(\vec{r})} + \frac{\partial E_{xc}}{\partial n(\vec{r})} \right) \delta n(\vec{r}) = 0$$

at the minimum

$$\frac{\partial J}{\partial n(\vec{r})} = v_J(\vec{r}) = \int d^3\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad \text{is the Hartree potential}$$

$$\frac{\partial E_{xc}}{\partial n(\vec{r})} = v_{xc}(\vec{r}) \quad \text{is the exchange-correlation potential}$$

- but $n(\vec{r})$ also minimizes $E_s[n]$, the energy of a system of N non-interacting electrons in an external potential $v_s(\vec{r})$

$$\begin{aligned} E_s[n] &= \sum_i \langle \phi_i | -\frac{1}{2} \nabla^2 + v_s | \phi_i \rangle \\ &= T_s[n] + \int d^3\vec{r} v_s(\vec{r}) n(\vec{r}) \end{aligned}$$

and for a variation $\delta n(\vec{r})$ of $n(\vec{r})$

$$\delta E_s = \delta T_s + \int d^3\vec{r} v_s(\vec{r}) \delta n(\vec{r}) = 0 \quad \text{at the minimum}$$

- equating δT_s in δE and δE_s , one gets

$$v_s(\vec{r}) = v(\vec{r}) + \int d^3\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + v_{xc}(\vec{r})$$

- Finally the total energy can be written

$$E_s[n] = \sum_{i=1}^N \epsilon_i = T_s[n] + \int d^3\vec{r} v_s(\vec{r}) n(\vec{r})$$

$$E[n] = T_s[n] + \int d^3\vec{r} v(\vec{r}) n(\vec{r}) + J[n] + E_{xc}[n]$$

$$= \sum_{i=1}^N \epsilon_i + \int d^3\vec{r} (v(\vec{r}) - v_s(\vec{r})) n(\vec{r}) + J[n] + E_{xc}[n]$$

$$E[n] = \sum_{i=1}^N \epsilon_i - J[n] + E_{xc}[n] - \int d^3\vec{r} n(\vec{r}) \frac{\partial E_{xc}[n]}{\partial n(\vec{r})} \quad (4)$$

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Local density approximation

approximate the xc energy by

$$E_{xc}^{LDA} = \int d^3\vec{r} \epsilon_{xc}(n(\vec{r})) \times n(\vec{r})$$

$\epsilon_{xc}(n)$ is the exchange and correlation energy **per electron** of the homogeneous electron gas with density n

$$\epsilon_{xc}(n) = \epsilon_x(n) + \epsilon_c(n)$$

$\epsilon_x(n)$: Dirac exchange energy

$$\epsilon_x(n) = C_x n^{\frac{1}{3}} ; C_x = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}}$$

(when added to the TF functional, give the Thomas-Fermi-Dirac functional)

$\epsilon_c(n)$:

fit to a quantum Monte-Carlo calculation (Ceperley-Alder)
two parametrisations using Padé approximants (Volsko, Wilk,
Nussair and Perdew-Zunger)

Some exact relations for atoms

1. exponential decay

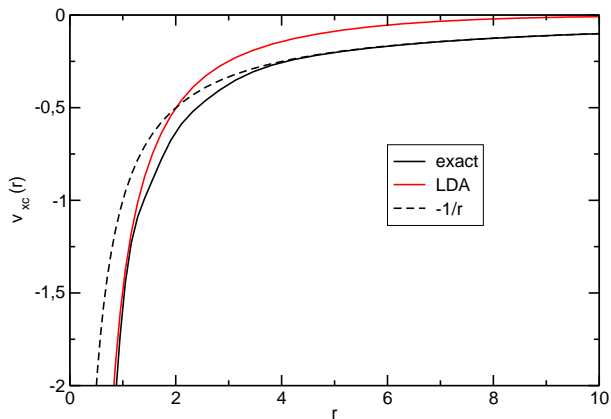
$$\sqrt{n(r)} \rightarrow Ar^\beta e^{-\sqrt{2I}r}$$

2. leads to condition on v_{xc} :

$$v_{xc}(r) \rightarrow -\frac{1}{r} \quad (r \rightarrow \infty)$$

3. determines KS HOMO : $\epsilon_{HOMO} = -I$

exchange-correlation potential for Be atom



courtesy of A. Savin

Generalized gradient approximation

From 1965 till 1986 : dark ages of DFT. Determination of exact results.

GGA :

$$E_{xc}[n] = \int d^3\vec{r} e_{xc}(n(\vec{r})) \times F(s(\vec{r}))$$

$$s = \frac{|\nabla n|}{2k_F n}; k_F = (3\pi^2 n)^{1/3}$$

Most used for molecular systems : BLYP (fit to closed shell atoms) separates exchange (B88) and correlation (LYP)

Also common are GGA's due to Perdew (ab initio) : P86, PW91, PBE

Largely correct for LDA overbinding

LDA	$\approx 1 \text{ eV}$
PBE	$\approx 1/3 \text{ eV}$
BLYP	$\approx 1/6 \text{ eV}$

Some defects of common functionals

- ▶ lack of long distance dispersion (vdW term $\propto \frac{1}{r^6}$)
- ▶ self-interaction error
- ▶ stretch H_2
- ▶ Derivative discontinuity and Fe^{2+} - Fe^{3+} problem

Functional zoology

LDA

GGA PBE, revPBE, PW91, BP86, BLYP, HCTCH etc.

Meta-GGA TPSS

Hybrid B3LYP, PBE0

...

For further reading I



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