Introduction to density-functional theory

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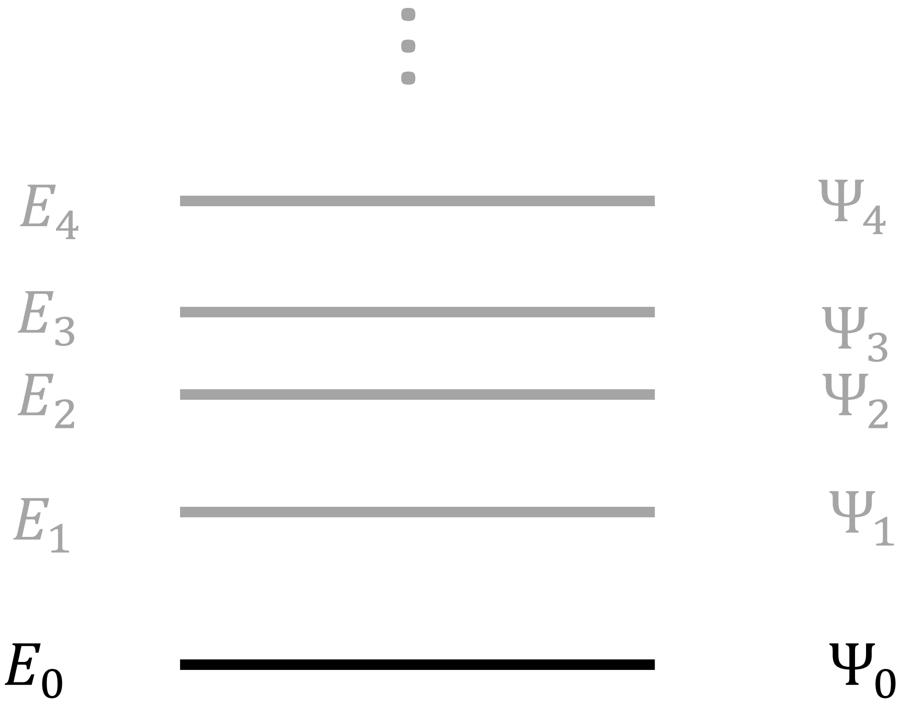
M2 lecture, Strasbourg, France.

Schrödinger equation for the *ground* state



$$\boxed{\hat{H}\Psi_0 = E_0\Psi_0}$$

N-electron Schrödinger equation for the *ground* state

$$\boxed{\hat{H}\Psi_0 = E_0\Psi_0}$$

where $\Psi_0 \equiv \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$, $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i) \equiv (x_i, y_i, z_i, \sigma_i = \pm\frac{1}{2})$ for $i = 1, 2, \ldots, N$,

and $\hat{H} = \hat{T} + \hat{W}_{\mathrm{ee}} + \hat{V}$.

$\hat{T} \equiv -\dfrac{1}{2}\displaystyle\sum_{i=1}^{N} \nabla^2_{\mathbf{r}_i} = -\dfrac{1}{2}\sum_{i=1}^{N}\left(\dfrac{\partial^2}{\partial x_i^2} + \dfrac{\partial^2}{\partial y_i^2} + \dfrac{\partial^2}{\partial z_i^2}\right)$ ⟶ *universal* kinetic energy operator

$\hat{W}_{\mathrm{ee}} \equiv \displaystyle\sum_{i<j}^{N} \dfrac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$ ⟶ *universal* two-electron repulsion operator

$\hat{V} \equiv \displaystyle\sum_{i=1}^{N} v(\mathbf{r}_i) \times$ where $v(\mathbf{r}) = -\displaystyle\sum_{A}^{\text{nuclei}} \dfrac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$ ⟶ local *nuclear* potential operator

(Fictitious) non-interacting electrons

- Solving the Schrödinger equation for non-interacting electrons is *easy*.
- You “just" have to solve the Schrödinger equation for a *single electron*.

$$\left(\hat{T}+\sum_{i=1}^{N}v(\mathbf{r}_i)\times\right)\Phi_0=\mathcal{E}_0\Phi_0 \quad \Leftrightarrow \quad \left[-\frac{1}{2}\nabla^2_{\mathbf{r}}+v(\mathbf{r})\times\right]\varphi_i(\mathbf{x})=\varepsilon_i\varphi_i(\mathbf{x}), \quad i=1,2,\ldots,N.$$

Proof: a *simple solution* to the N-electron non-interacting Schrödinger equation is

$$\Phi_0\equiv\varphi_1(\mathbf{x}_1)\times\varphi_2(\mathbf{x}_2)\times\ldots\times\varphi_N(\mathbf{x}_N)=\prod_{j=1}^{N}\varphi_j(\mathbf{x}_j) \qquad \leftarrow \textit{Hartree product!}$$

since $\left(\hat{T}+\sum_{i=1}^{N}v(\mathbf{r}_i)\times\right)\Phi_0=\sum_{i=1}^{N}\prod_{j\neq i}^{N}\varphi_j(\mathbf{x}_j)\times\left[-\frac{1}{2}\nabla^2_{\mathbf{r}_i}+v(\mathbf{r}_i)\times\right]\varphi_i(\mathbf{x}_i)=\left(\sum_{i=1}^{N}\varepsilon_i\right)\Phi_0.$

(Real) interacting many-electron problem

- Before addressing the true (interacting) problem we should keep in mind that electrons are *fermions*.
- Consequently, they should be described by *Slater determinants* instead of Hartree products.
- Therefore, in the particular case of *two electrons*, we have

$$\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) \quad \longrightarrow \quad \Phi_0 \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \Big[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1)\Big].$$

- When computing the two-electron repulsion energy $\left\langle \Phi_0 \middle| \hat{W}_{\mathrm{ee}} \middle| \Phi_0 \right\rangle$ we describe the so-called *Hartree* (i.e. electrostatic) and *exchange* energies.
- Finally, Φ_0 *cannot* be the exact solution to the interacting Schrödinger equation [whatever choice is made for the spin-orbitals $\{\varphi_i(\mathbf{x})\}_{i=1,2,\ldots}$].
- The energy contribution that is missing is referred to as *correlation* energy.

Mapping the interacting problem onto a non-interacting one

- Is it possible to *extract* the exact (interacting) ground-state energy E_0 *from a non-interacting system*?

- If yes, then it would lead to a huge *simplification* of the problem.

- Nevertheless, the question sounds a bit weird since the two-electron repulsion is completely ignored in a non-interacting system.

- One way to establish a *connection* between interacting and non-interacting worlds is to use the *electron density* as basic variable (instead of the wavefunction).

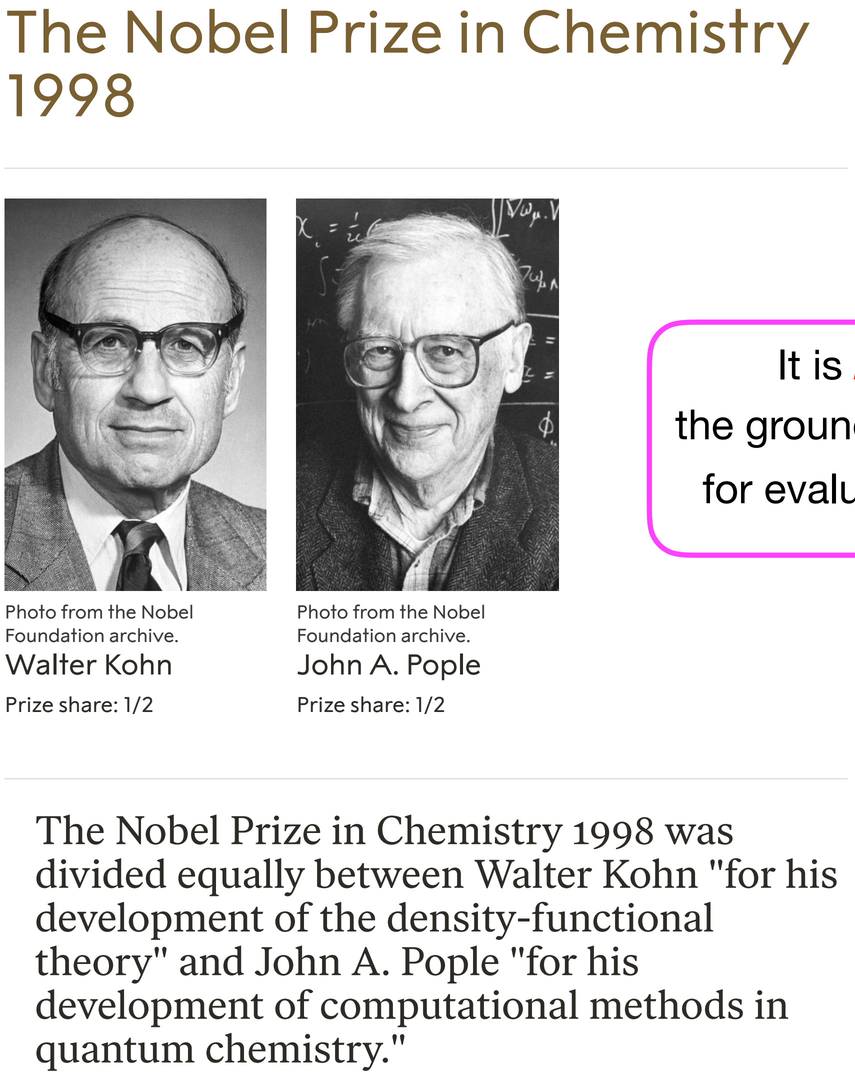
- Electron density for a *non-interacting* system: $n_{\Phi_0}(\mathbf{r}) = \sum_{\sigma=\pm\frac{1}{2}} \sum_{i=1}^{N} \left|\varphi_i(\mathbf{r},\sigma)\right|^2$

- Electron density for an *interacting* system:

$$n_{\Psi_0}(\mathbf{r}) = N \sum_{\sigma=\pm\frac{1}{2}} \int \mathrm{d}\mathbf{x}_2 \ldots \int \mathrm{d}\mathbf{x}_N \left|\Psi_0(\mathbf{r},\sigma,\mathbf{x}_2,\ldots,\mathbf{x}_N)\right|^2$$

- The so-called *Kohn–Sham* non-interacting system (from which E_0 can be determined) is such that $\boxed{n_{\Phi_0}(\mathbf{r}) = n_{\Psi_0}(\mathbf{r})}$.

Density-functional theory (DFT)



The Nobel Prize in Chemistry 1998

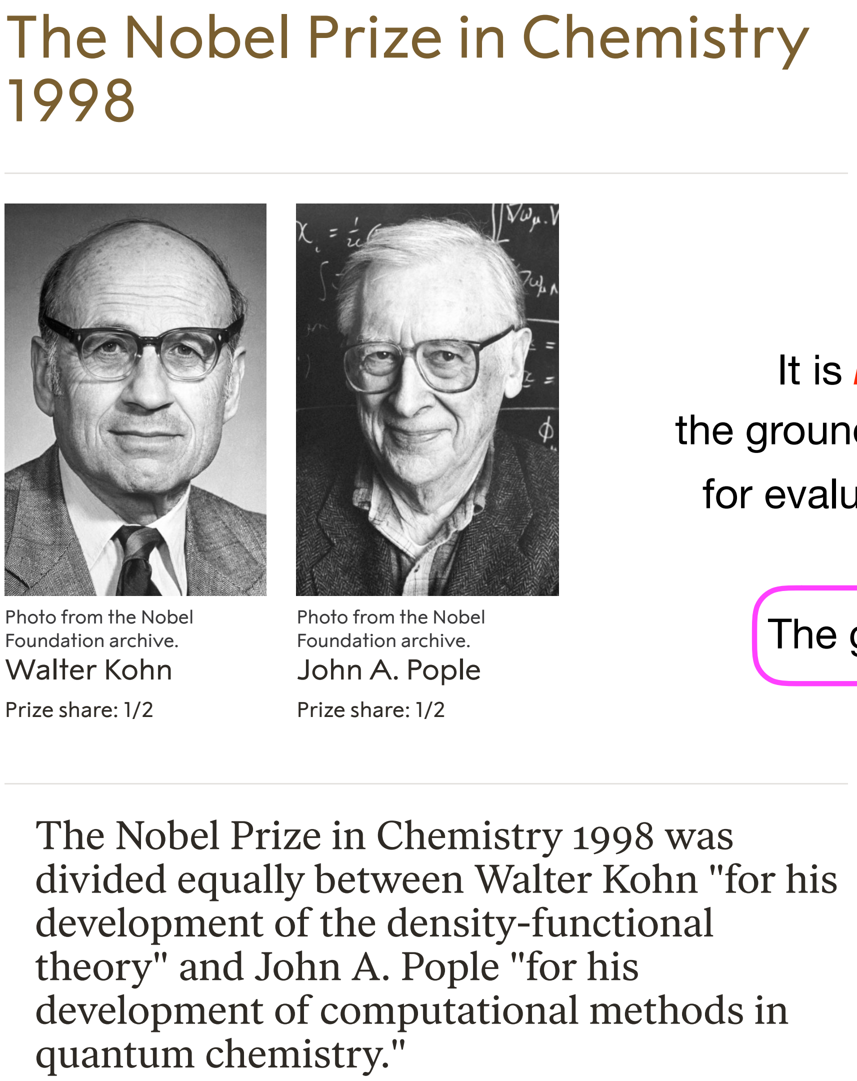
Photo from the Nobel Foundation archive.
Walter Kohn
Prize share: 1/2

Photo from the Nobel Foundation archive.
John A. Pople
Prize share: 1/2

The Nobel Prize in Chemistry 1998 was divided equally between Walter Kohn "for his development of the density-functional theory" and John A. Pople "for his development of computational methods in quantum chemistry."

It is ***in principle unnecessary to know***
the ground-state many-electron ***wave function*** Ψ_0
for evaluating the exact ground-state energy E_0.

Density-functional theory (DFT)



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It is ***in principle unnecessary to know***
the ground-state many-electron ***wave function*** Ψ_0
for evaluating the exact ground-state energy E_0.

The ground-state ***density*** n_0 is ***sufficient.***

An important observation to make before we start...

The *one-electron potential energy* is an *explicit functional of the density*:

$$\boxed{\left\langle \Psi \middle| \sum_{i=1}^{N} v(\mathbf{r}_i)\times \middle| \Psi \right\rangle = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\; v(\mathbf{r}) n_\Psi(\mathbf{r}) \overset{notation}{\equiv} (v|n_\Psi)}$$

Levy's constrained search formalism

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

Levy's constrained search formalism

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \min_{n} \left\{ \boxed{\min_{\Psi \rightarrow n}} \langle \Psi | \hat{H} | \Psi \rangle \right\}$$

$$\downarrow$$

Pre-minimisation over wave functions Ψ
that have the ***same density*** $n_{\Psi}(\mathbf{r}) = n(\mathbf{r})$

*Levy M (1979) Proc Natl Acad Sci USA **76**(12):6062*

Levy's constrained search formalism

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \boxed{\min_{n}} \left\{ \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle \right\}$$

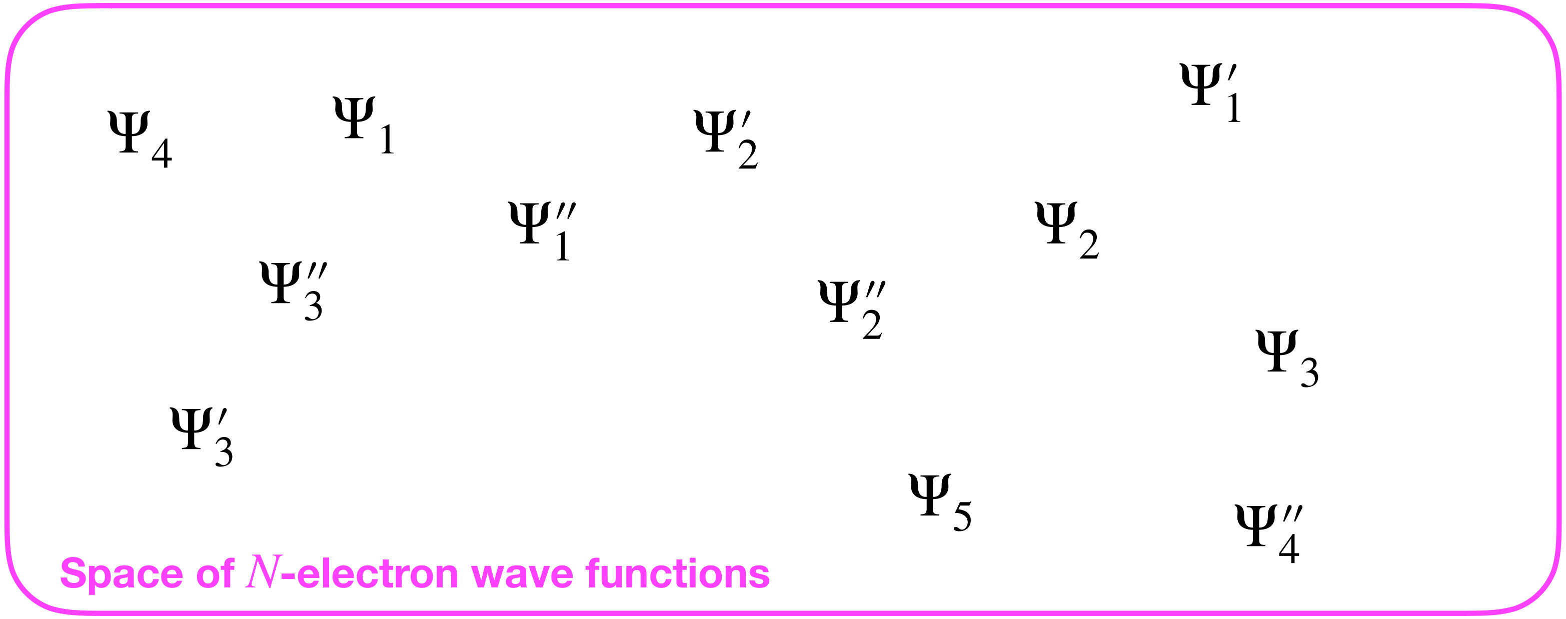
$\downarrow$

Minimisation over ***densities*** n

*Levy M (1979) Proc Natl Acad Sci USA **76**(12):6062*

Levy's constrained search formalism

$$
\begin{aligned}
E_0 &= \boxed{\min_{\Psi}} \langle \Psi | \hat{H} | \Psi \rangle \\
&= \min_{n} \left\{ \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle \right\}
\end{aligned}
$$



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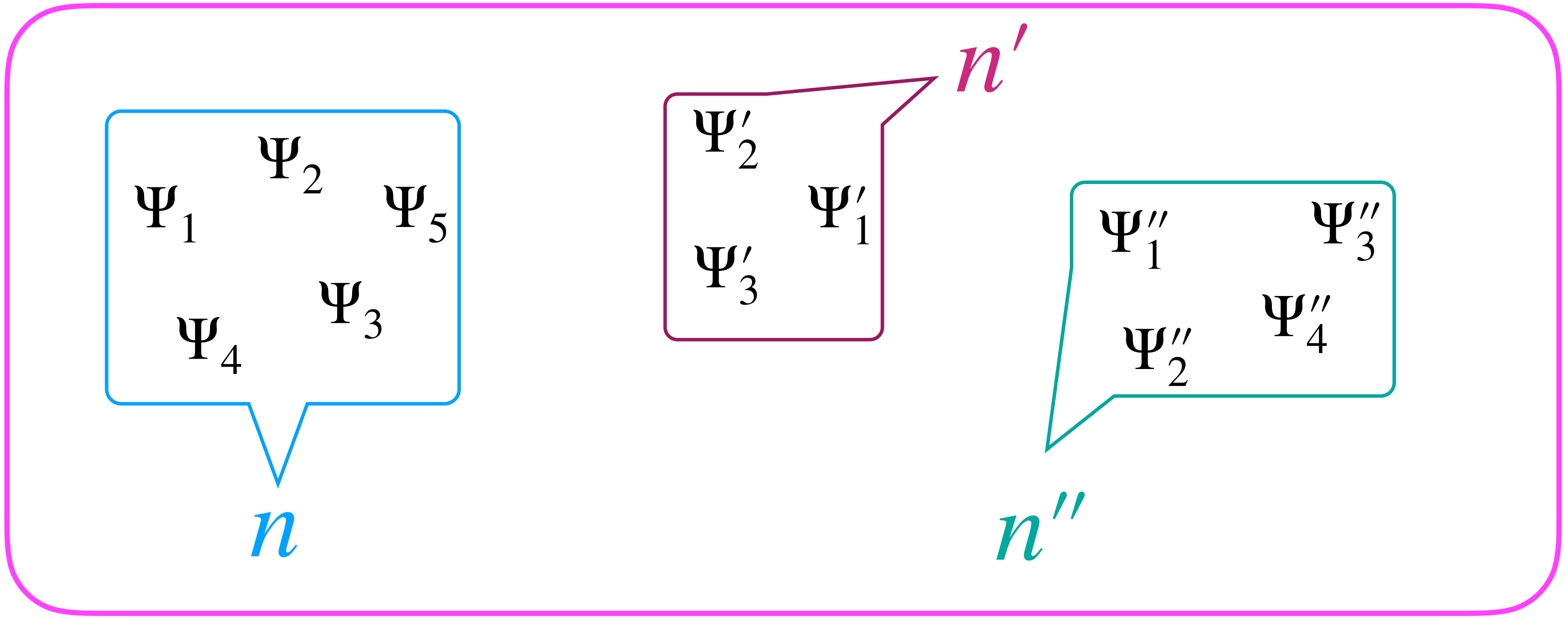
Levy's constrained search formalism

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \boxed{\min_{n} \left\{ \min_{\Psi \to n} \right.} \left. \langle \Psi | \hat{H} | \Psi \rangle \right\}$$



Levy M (1979) Proc Natl Acad Sci USA ***76***(12):6062

Levy's constrained search formalism

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \min_{n} \left\{ \min_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle \right\}$$

$$\hat{H} = \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$$

$$= \min_{n} \left\{ \min_{\Psi \rightarrow n} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\rm ee} | \Psi \rangle + \int d\mathbf{r}\, v(\mathbf{r}) n_{\Psi}(\mathbf{r}) \right\} \right\}$$

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

$$\hat{W}_{\rm ee} \equiv \frac{1}{2} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Levy's constrained search formalism

$$E_0 = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle$$

$$= \min_{n} \left\{ \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle \right\}$$

$$= \min_{n} \left\{ \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle + \int d\mathbf{r}\, v(\mathbf{r}) n_{\Psi}(\mathbf{r}) \right\} \right\}$$

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Levy's constrained search formalism

$$
\begin{aligned}
E_0 &= \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \\
&= \min_{n} \left\{ \min_{\Psi \to n} \langle \Psi | \hat{H} | \Psi \rangle \right\} \\
&= \min_{n} \left\{ \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle + \int d\mathbf{r}\, v(\mathbf{r}) n_{\Psi}(\mathbf{r}) \right\} \right\} \\
&= \min_{n} \left\{ \boxed{\min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \right\}} + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\} \\
&= \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}
\end{aligned}
$$

Levy's constrained search formalism

$$E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}$$

*We recover the **Hohenberg-Kohn variational principle** of DFT!*

P. Hohenberg and W. Kohn, Phys. Rev. ***136****, B864 (1964)*

Kohn-Sham DFT formalism

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \xrightarrow{\text{Kohn-Sham}} T_{\mathrm{s}}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} | \Psi \rangle$$

Interacting universal functional

Non-interacting
(kinetic energy) functional

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Kohn-Sham DFT formalism

$$F[n] = \min_{\Psi\rightarrow n} \langle \Psi | \hat{T} + \hat{W}_{\text{ee}} | \Psi \rangle \xrightarrow{\text{Kohn-Sham}} T_{\text{s}}[n] = \min_{\Psi\rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle$$

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Non-interacting
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$$F[n] - T_{\text{s}}[n] = E_{\text{Hxc}}[n]$$

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Kohn-Sham DFT formalism

$$F[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} | \Psi \rangle \xrightarrow{\text{Kohn-Sham}} T_{\mathrm{s}}[n] = \min_{\Psi \to n} \langle \Psi | \hat{T} | \Psi \rangle$$

Interacting universal functional

Non-interacting
(kinetic energy) functional

$$F[n] - T_{\mathrm{s}}[n] = E_{\mathrm{Hxc}}[n]$$

$$= E_{\mathrm{H}}[n] + E_{\mathrm{xc}}[n]$$

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Kohn-Sham DFT formalism

Hartree *density functional*

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

Electrostatics
(evaluated with quantum electron densities)

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Kohn-Sham DFT formalism

Hartree *density functional*

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

← ***Electrostatics***
(evaluated with quantum electron densities)

Exchange-correlation (xc) *density functional*

$$E_{\mathrm{xc}}[n] = F[n] - T_{\mathrm{s}}[n] - E_{\mathrm{H}}[n]$$

← ***Quantum***
many-electron effects

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Kohn-Sham DFT formalism

Hartree *density functional*

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

← ***Electrostatics***
(evaluated with quantum electron densities)

Exchange-correlation (xc) *density functional*

$$E_{\mathrm{xc}}[n] = ???$$

← ***Quantum***
many-electron effects

The ***exact*** *xc functional is* ***uniquely defined*** *but*
many *(many)* ***approximations***
can be found in the literature (LDA, PBE, B3LYP, SCAN, …).

Variational principle
in Kohn-Sham DFT

$$E_0 = \min_n \left\{ F[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_n \left\{ T_s[n] + E_{\mathrm{Hxc}}[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_n \left\{ \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} | \Psi \rangle \right\} + E_{\mathrm{Hxc}}[n] + \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r}) \right\}$$

$$= \min_n \left\{ \min_{\Psi \to n} \left\{ \langle \Psi | \hat{T} | \Psi \rangle + E_{\mathrm{Hxc}}[n_\Psi] + \int d\mathbf{r}\, v(\mathbf{r}) n_\Psi(\mathbf{r}) \right\} \right\}$$

$$= \min_n \left\{ \min_{\Psi \to n} \left\{ \langle \Psi | \hat{H} - \hat{W}_{\mathrm{ee}} | \Psi \rangle + E_{\mathrm{Hxc}}[n_\Psi] \right\} \right\}$$

$$= \min_\Psi \left\{ \langle \Psi | \hat{H} - \hat{W}_{\mathrm{ee}} | \Psi \rangle + E_{\mathrm{Hxc}}[n_\Psi] \right\}$$

Comparing variational principles

$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{H} | \Psi \rangle \right\} = \min_{\Psi} \left\{ \langle \Psi | \hat{H} - \hat{W}_{\rm ee} | \Psi \rangle + E_{\rm Hxc}[n_{\Psi}] \right\}$$

Comparing variational principles

$$E_0 = \boxed{\min_{\Psi}\left\{\langle\Psi|\hat{H}|\Psi\rangle\right\}} = \min_{\Psi}\left\{\langle\Psi|\hat{H}-\hat{W}_{\mathrm{ee}}|\Psi\rangle+E_{\mathrm{Hxc}}[n_{\Psi}]\right\}$$

$\downarrow$

Pure ***wave function theory*** *(WFT)*

Comparing variational principles

$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{H} | \Psi \rangle \right\} = \boxed{\min_{\Psi} \left\{ \langle \Psi | \hat{H} - \hat{W}_{\mathrm{ee}} | \Psi \rangle + E_{\mathrm{Hxc}}[n_{\Psi}] \right\}}$$

Kohn-Sham DFT

Comparing variational principles

$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{H} | \Psi \rangle \right\} = \boxed{\min_{\Psi} \left\{ \langle \Psi | \hat{H} - \hat{W}_{\mathrm{ee}} | \Psi \rangle + E_{\mathrm{Hxc}}[n_{\Psi}] \right\}}$$

Explicit *two-electron repulsions*
are ***removed*** *from the Hamiltonian…*

Comparing variational principles

$$E_0 = \min_{\Psi}\left\{\langle\Psi|\hat{H}|\Psi\rangle\right\} = \boxed{\min_{\Psi}\left\{\langle\Psi|\hat{H}-\hat{W}_{\rm ee}|\Psi\rangle+E_{\rm Hxc}[n_{\Psi}]\right\}}$$

***Explicit** two-electron repulsions are **removed** from the Hamiltonian…*

*… and treated **implicitly** as functionals of the density.*

Comparing variational principles

$$E_0 = \min_{\Psi}\left\{\langle\Psi|\hat{H}|\Psi\rangle\right\} = \boxed{\min_{\Psi}\left\{\langle\Psi|\hat{H}-\hat{W}_{\mathrm{ee}}|\Psi\rangle+E_{\mathrm{Hxc}}[n_{\Psi}]\right\}}$$

Explicit *two-electron repulsions*
are ***removed*** *from the Hamiltonian…*

*The **one-electron picture** is made **exact** in KS-DFT!*

Comparing wave function theory (WFT) with KS-DFT

$$E_0 = \min_{\Psi} \left\{ \langle\Psi|\hat{T}+\hat{V}+\hat{W}_{\mathrm{ee}}|\Psi\rangle \right\} = \min_{\Phi} \left\{ \langle\Phi|\hat{T}+\hat{V}|\Phi\rangle + E_{\mathrm{Hxc}}[n_{\Phi}] \right\}$$

$\downarrow$ WFT

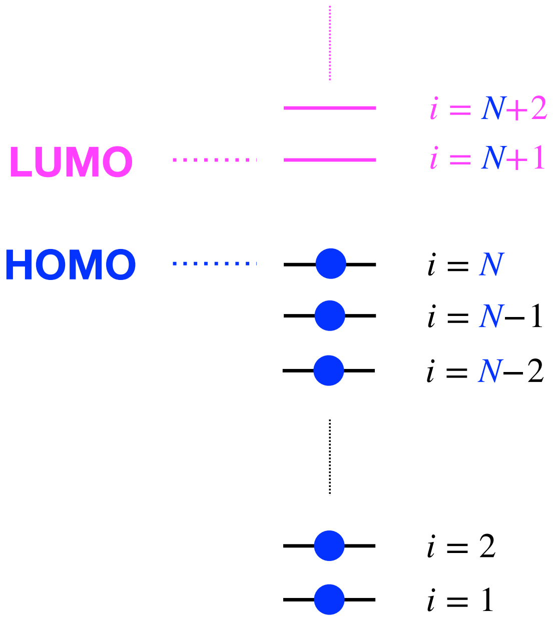
$\downarrow$ DFT

$$\Psi = \underbrace{\Phi^{\mathrm{HF}} + \sum_k C_k \mathrm{det}_k}_{\text{multideterminantal wave function}}$$

$$\Phi = \underbrace{|\varphi_1^2\varphi_2^2\ldots\varphi_{\frac{N}{2}}^2|}_{\text{single determinant}}$$

DFT for N-electron ground states

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2}+v(\mathbf{r})+v_{\mathrm{Hxc}}(\mathbf{r})\right]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$



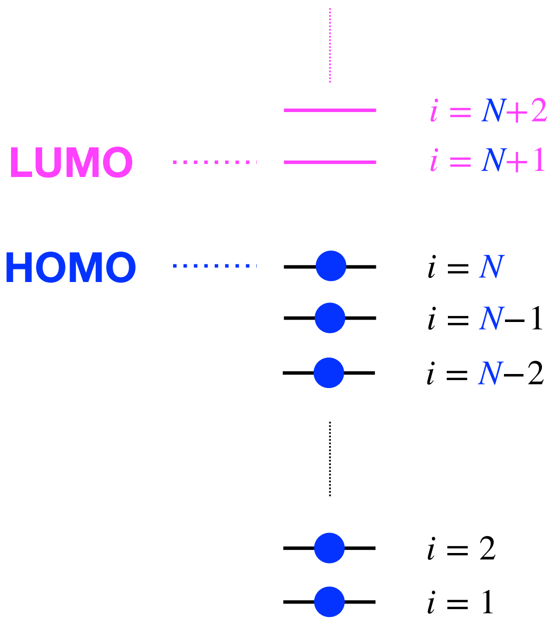
W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

DFT for N-electron ground states

$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2}+v(\mathbf{r})+v_{\rm Hxc}(\mathbf{r})\right]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$

$$\boxed{n_0(\mathbf{r})=\sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2}$$

exact ground-state ***density***



LUMO

HOMO

$i = N+2$

$i = N+1$

$i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

DFT for N-electron ground states

$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2}+v(\mathbf{r})+v_{\mathrm{Hxc}}(\mathbf{r})\right]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$

$$\boxed{n_0(\mathbf{r})=\sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2}$$

exact ground-state ***density***

$$v_{\mathrm{Hxc}}(\mathbf{r})=\left.\frac{\delta E_{\mathrm{Hxc}}[n]}{\delta n(\mathbf{r})}\right|_{n=n_0}$$

Hartree-exchange-correlation
local (multiplicative) ***potential***

W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Standard density-functional approximations (DFAs)

Local and semi-local functionals

$$E_{xc}[n] \approx \int d\mathbf{r}\, \varepsilon_{xc}\big(n(\mathbf{r})\big) \times n(\mathbf{r})$$

LDA *(uniform electron gas)*

*S. H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58 (8): 1200–1211 (**1980**).*

$$E_{xc}[n] \approx \int d\mathbf{r}\, \varepsilon_{xc}\big(n(\mathbf{r}), |\nabla n(\mathbf{r})|\big) \times n(\mathbf{r})$$

⋮

Generalized gradient approximations (GGAs):

LYP, PBE, …

*C. **L**ee, W. **Y**ang, and R. G. **P**arr. Phys. Rev. B, 57:785, (**1988**).*

*J. P. **P**erdew, K. **B**urke, M. **E**rnzerhof, Phys. Rev. Lett., 77, 3865 (**1996**).*

Hybrid functionals

Hartree-Fock-like exchange energy *(evaluated with KS orbitals)*

$$E_{xc}[n] \approx \alpha\boxed{E_x^{HF}[\Phi]} + (1-\alpha)E_x^{DFA}[n_\Phi] + E_c^{DFA}[n_\Phi]$$

B3LYP

*A. D. **B**ecke, J. Chem. Phys. 98, 1372 (**1993**).*

$$E_{xc}[n] \approx \boxed{E_x^{lr,HF}[\Phi] + E_x^{sr,DFA}[n_\Phi]} + E_c^{DFA}[n_\Phi]$$

⋮

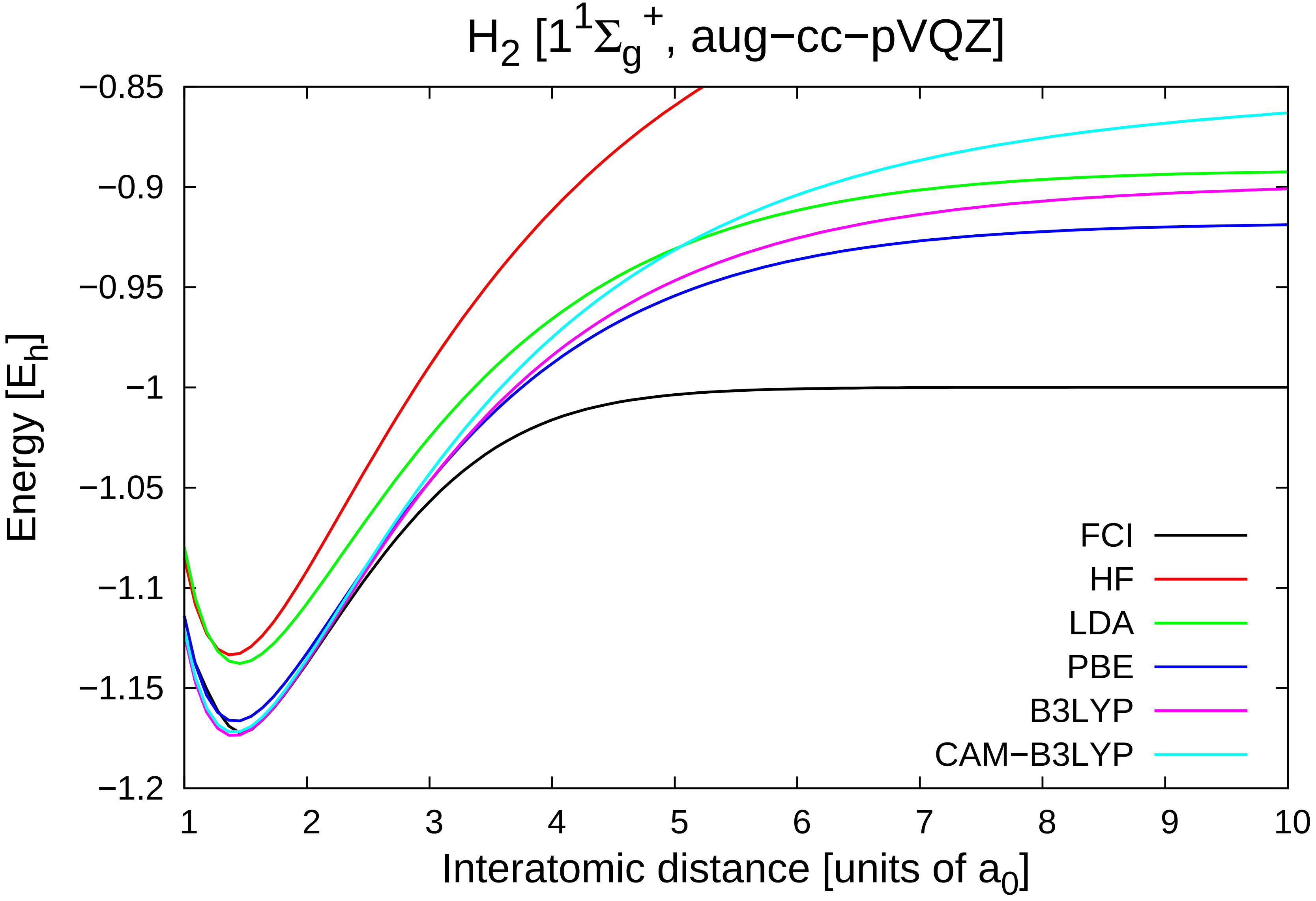
$$\hat{W}_{ee} = \hat{W}_{ee}^{lr} + \hat{W}_{ee}^{sr}$$

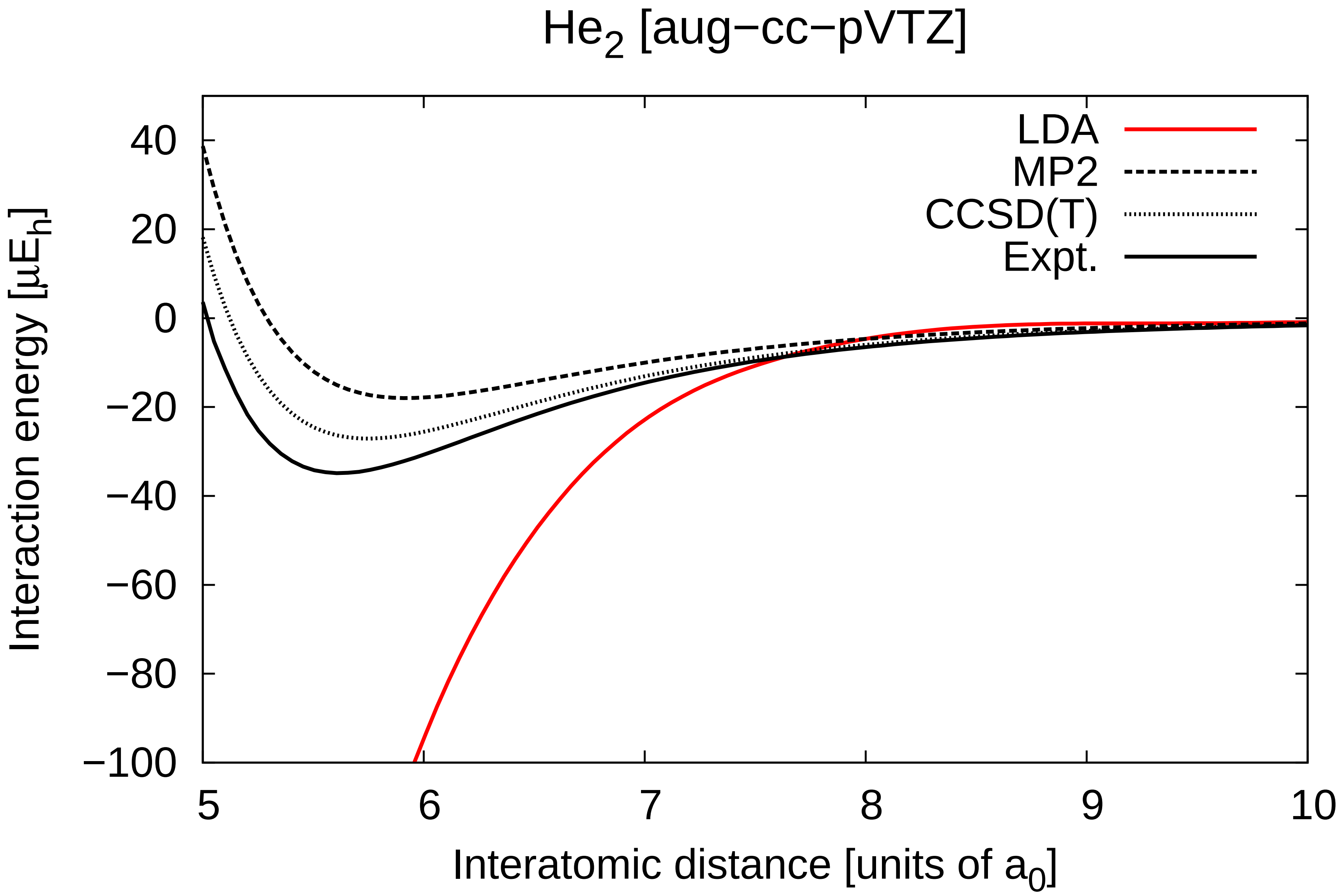
Long-range short-range

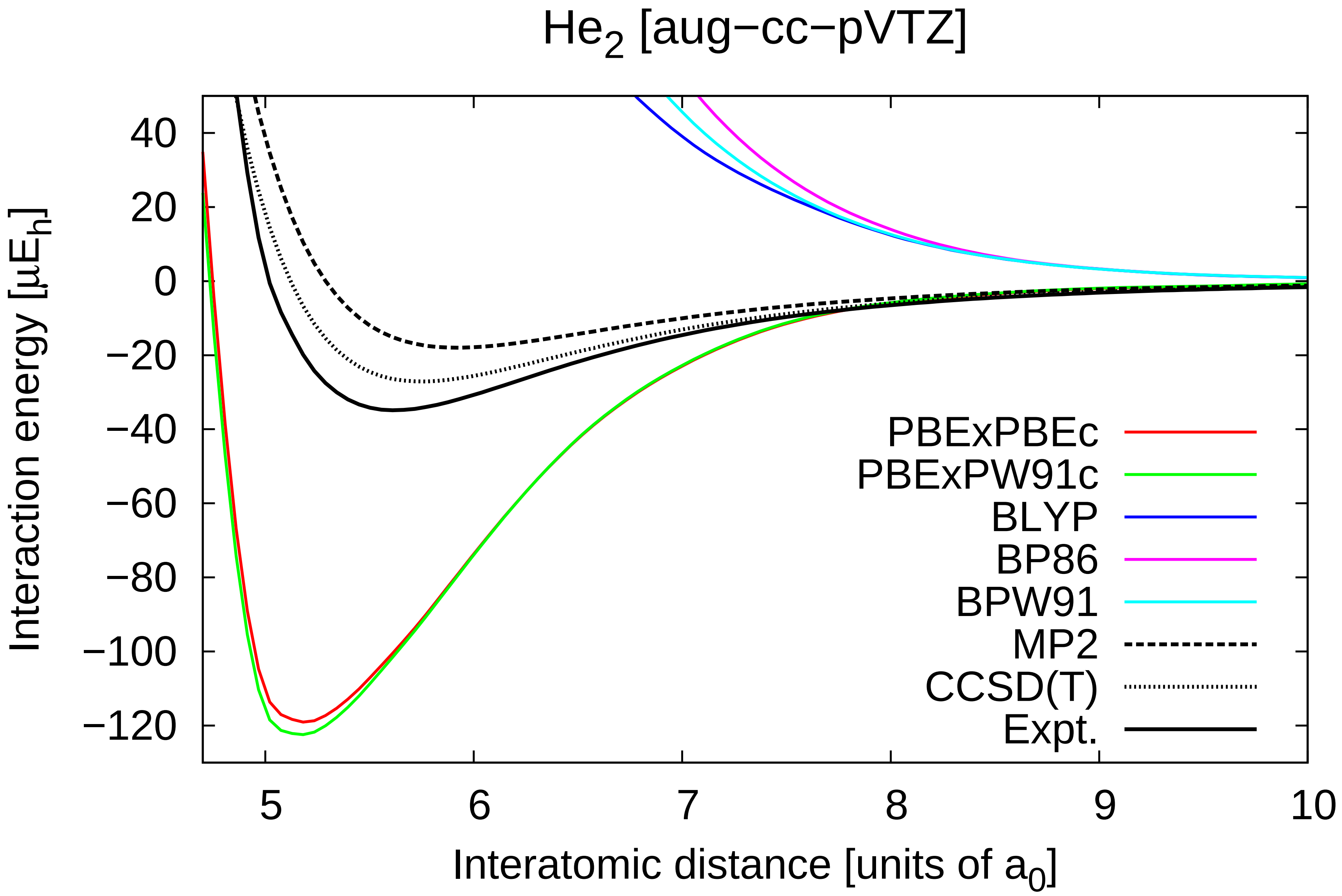
Range-separated hybrids

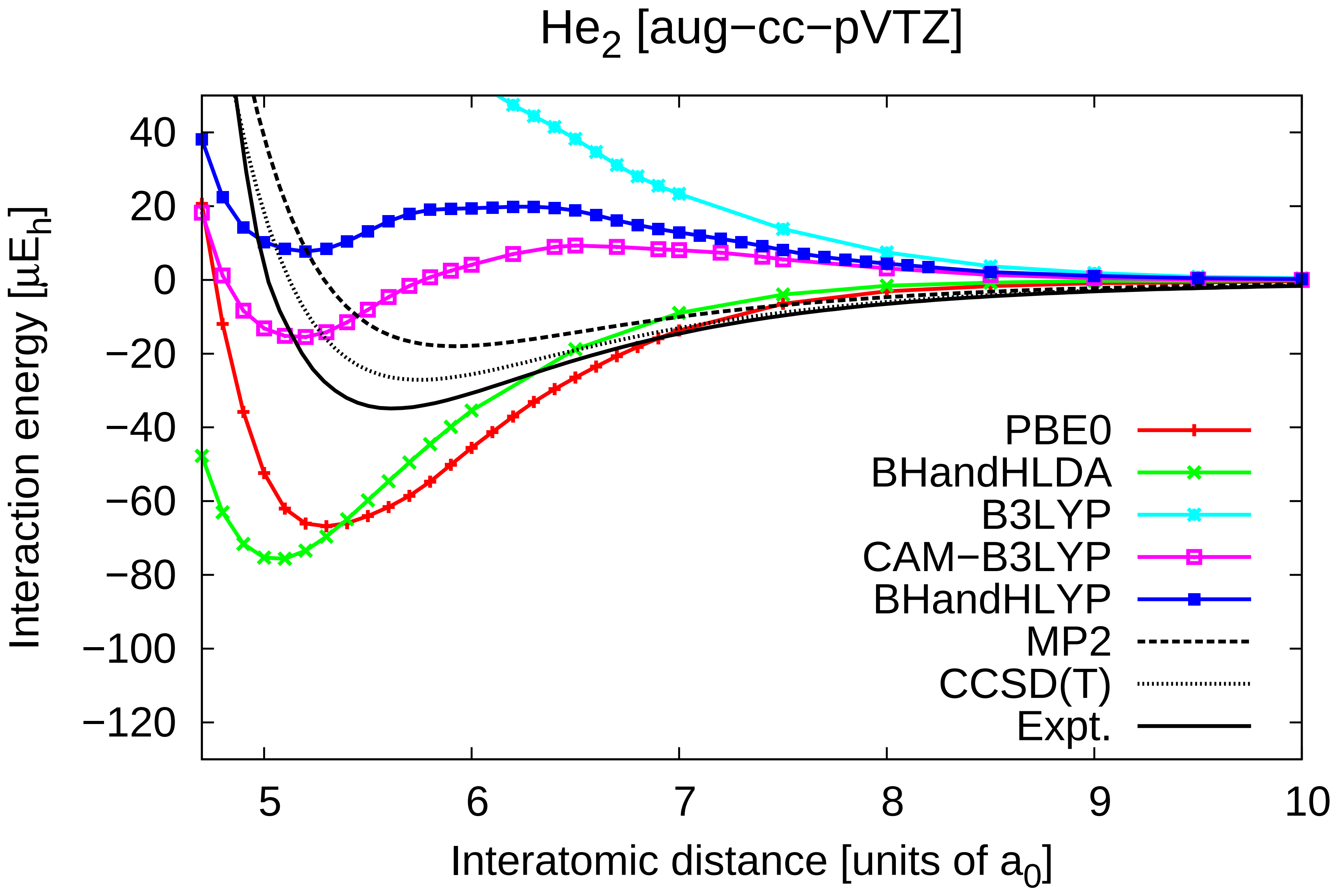
CAM-B3LYP

*Yanai, T.; Tew, D. P.; Handy, N. C., Chem. Phys. Lett., 393, 51-57 (**2004**).*


H_2 [$1^1\Sigma_g^+$, aug−cc−pVQZ]
Energy [E_h]
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
1
2
3
4
5
6
7
8
9
10
Interatomic distance [units of a_0]
FCI
HF
LDA
PBE
B3LYP
CAM−B3LYP


He2 [aug−cc−pVTZ]
Interaction energy [μEh]
Interatomic distance [units of a0]
40
20
0
−20
−40
−60
−80
−100
5
6
7
8
9
10
LDA
MP2
CCSD(T)
Expt.

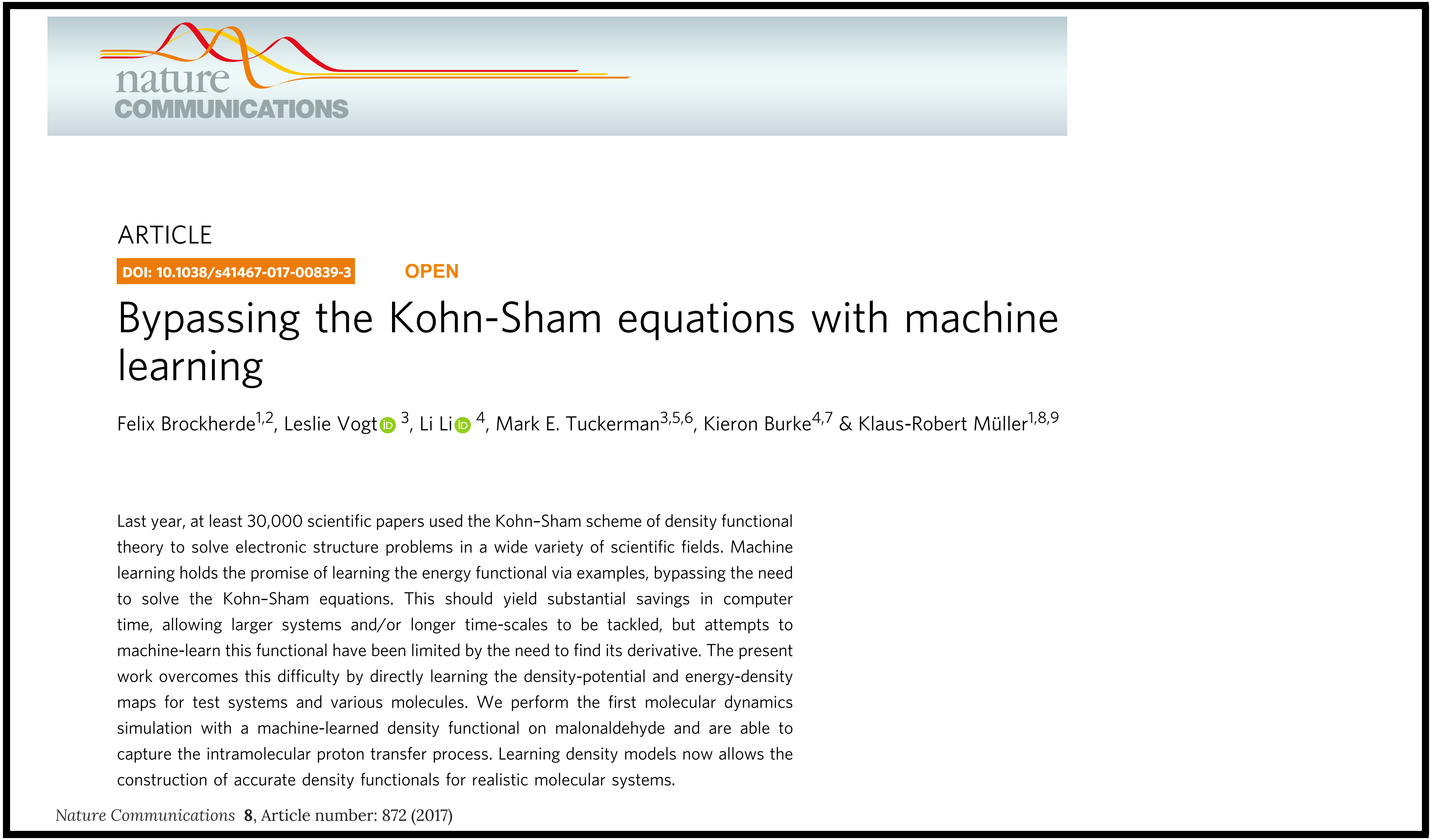

He$_2$ [aug−cc−pVTZ]
Interaction energy [μE$_h$]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
PBExPBEc
PBExPW91c
BLYP
BP86
BPW91
MP2
CCSD(T)
Expt.


He$_2$ [aug−cc−pVTZ]
Interaction energy [μE$_h$]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
PBE0
BHandHLDA
B3LYP
CAM−B3LYP
BHandHLYP
MP2
CCSD(T)
Expt.

DFT, us (humans), and the machines

$$n(\mathbf{r}) \quad \rightarrow \quad n_{\gamma}(\mathbf{r}) = \gamma^{3} n(\gamma \mathbf{r})$$

$$E_{\mathrm{x}}[n_{\gamma}] \quad = \quad \gamma E_{\mathrm{x}}[n]$$



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Bypassing the Kohn-Sham equations with machine learning

Felix Brockherde[1,2], Leslie Vogt [3], Li Li [4], Mark E. Tuckerman[3,5,6], Kieron Burke[4,7] & Klaus-Robert Müller[1,8,9]

Last year, at least 30,000 scientific papers used the Kohn–Sham scheme of density functional theory to solve electronic structure problems in a wide variety of scientific fields. Machine learning holds the promise of learning the energy functional via examples, bypassing the need to solve the Kohn–Sham equations. This should yield substantial savings in computer time, allowing larger systems and/or longer time-scales to be tackled, but attempts to machine-learn this functional have been limited by the need to find its derivative. The present work overcomes this difficulty by directly learning the density-potential and energy-density maps for test systems and various molecules. We perform the first molecular dynamics simulation with a machine-learned density functional on malonaldehyde and are able to capture the intramolecular proton transfer process. Learning density models now allows the construction of accurate density functionals for realistic molecular systems.

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Teaching the HK theorem to a machine

- One can *teach the functional* $T_{\rm s}[n]$ to a machine.
- But then it needs to find the value of $\delta T_{\rm s}[n]/\delta n(\mathbf{r})$ by itself ...
- ... in order to determine n_{Ψ_0} variationally from $v = v_{\rm ne}$ (*i.e*, the nuclear potential energy of the *molecule under study*).
- What about *learning the ground-state density map* $v \rightarrow n_0[v]$ directly?*
- If we have $v_{\rm ne}$, the machine will tell us directly what the ground-state density $n_{\Psi_0} = n_0[v_{\rm ne}]$ is.
- We can also *teach* the machine how to *compute the energy*:

$$E[n_{\Psi_0}] = T_{\rm s}[n_{\Psi_0}] + E_{\rm Hxc}[n_{\Psi_0}] + (v_{\rm ne}|n_{\Psi_0}).$$

* Brockherde, Felix, Vogt, Leslie, Li ,Li, Tuckerman, Mark E, Burke, Kieron and Muller, Klaus-Robert, *Nature Communications* 8, 872 (2017).

Teaching the HK theorem to a machine

- *Expansion* of densities in an *orthonormal* basis of functions $\{\phi_l(\mathbf{r})\}_{1\leq l\leq L}$:

$$n_0[v](\mathbf{r}) = \sum_{l=1}^{L} u^{(l)}[v] \times \phi_l(\mathbf{r}).$$

- Kernel Ridge Regression (KRR) method:

$$u^{(l)}[v] = \sum_{j=1}^{M} \beta_j^{(l)} \times k\left(v, v_j\right)$$

$$k(v, v_i) = \exp\left(-\frac{\int d\mathbf{r}\left|v(\mathbf{r}) - v_i(\mathbf{r})\right|^2}{2\sigma^2}\right)$$

where $\{v_j\}_{1\leq j\leq M}$ are the potentials the machine will learn from.

Brockherde, Felix, Vogt, Leslie, Li ,Li, Tuckerman, Mark E, Burke, Kieron and Muller, Klaus-Robert, *Nature Communications* 8, 872 (2017).

Teaching the HK theorem to a machine

- The machine will *learn about each ground-state density* (M densities will be considered in total)

$$n_i(\mathbf{r}) = \sum_{l=1}^{L} u_i^{(l)} \times \phi_l(\mathbf{r})$$

  that has been calculated for a given potential $v_i(\mathbf{r})$. The learning process relies on the previously introduced KRR method:

$$n_0[v_i](\mathbf{r}) = \sum_{l=1}^{L} u^{(l)}[v_i] \times \phi_l(\mathbf{r})$$

$$u^{(l)}[v_i] = \sum_{j=1}^{M} \beta_j^{(l)} \times k\left(v_i, v_j\right)$$

$$k(v_i, v_j) = \exp\left(-\frac{\int d\mathbf{r} \left|v_i(\mathbf{r}) - v_j(\mathbf{r})\right|^2}{2\sigma^2}\right)$$

- The paramaters to be *optimized* (learning process) are $\boldsymbol{\beta} \equiv \left\{\beta_j^{(l)}\right\}_{1\leq j\leq M, 1\leq l\leq L}$.

Teaching the HK theorem to a machine

- The machine will *learn about each ground-state density* (M densities will be considered in total)

$$n_i(\mathbf{r}) = \sum_{l=1}^{L} \boxed{u_i^{(l)}} \times \phi_l(\mathbf{r})$$

that has been calculated for a given potential $v_i(\mathbf{r})$. The learning process relies on the previously introduced KRR method:

$$n_0[v_i](\mathbf{r}) = \sum_{l=1}^{L} \boxed{u^{(l)}[v_i]} \times \phi_l(\mathbf{r})$$

$$\boxed{u^{(l)}[v_i]} = \sum_{j=1}^{M} \beta_j^{(l)} \times \boxed{k\left(v_i, v_j\right)}$$

$$\boxed{k\left(v_i, v_j\right)} = \exp\left(-\frac{\int d\mathbf{r}\Big|v_i(\mathbf{r}) - v_j(\mathbf{r})\Big|^2}{2\sigma^2}\right)$$

- Naive learning process: $k\left(v_i, v_j\right) \approx \delta_{ij} \quad \Rightarrow \quad \beta_i^{(l)} = u_i^{(l)}$.

Teaching the HK theorem to a machine

- Cost function to be minimized with respect to $\boldsymbol{\beta}$:

$$
\begin{aligned}
e\left(\boldsymbol{\beta}\right) &= \sum_{i=1}^{M}\int d\mathbf{r}\,\left|n_i(\mathbf{r}) - n_0[v_i](\mathbf{r})\right|^2 \\
&\overset{\textit{orthonormal basis}}{=} \sum_{i=1}^{M}\sum_{l=1}^{L}\left|u_i^{(l)} - u^{(l)}[v_i]\right|^2 \\
&= \sum_{i=1}^{M}\sum_{l=1}^{L}\left|u_i^{(l)} - \sum_{j=1}^{M}\beta_j^{(l)} \times k\left(v_i, v_j\right)\right|^2
\end{aligned}
$$

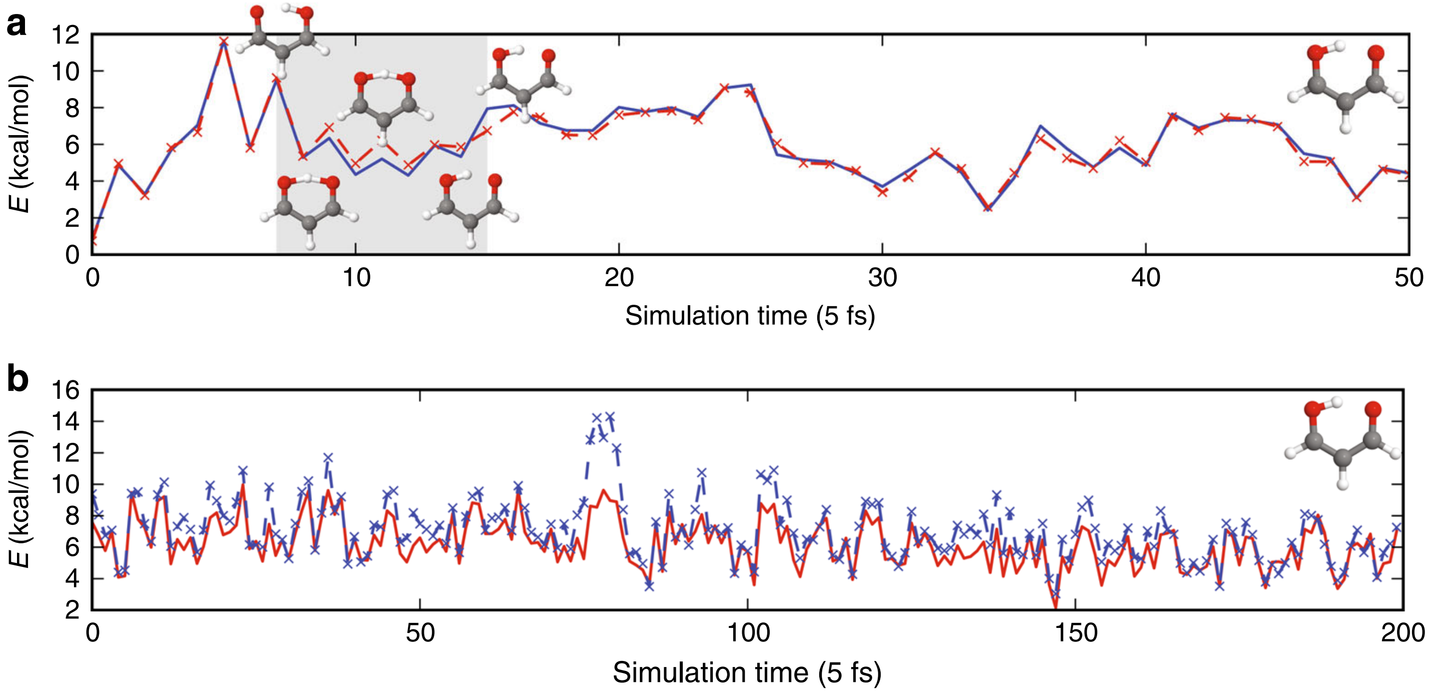

Fig. 5 Energy errors of ML-HK along ab initio MD and ML-generated trajectories. **a** Energy errors of ML-HK along a 0.25 ps ab initio MD trajectory of malonaldehyde. PBE values in *blue*, ML-HK values in *red*. The ML model correctly predicts energies during proton transfer in frames 7–15 without explicit inclusion of these geometries in the training set. **b** Energy errors of ML-HK along a 1 ps MD trajectory of malonaldehyde generated by the ML-HK model. ML-HK values in *red*, PBE values of trajectory snapshots in *blue*

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