Introduction to density-functional theory

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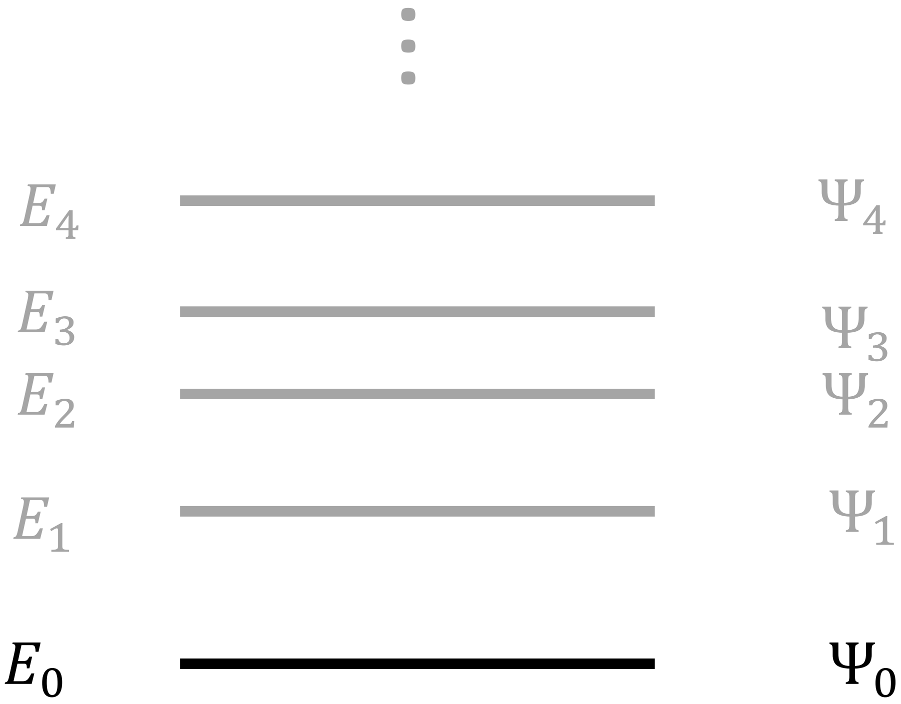
Schrödinger equation for the *ground* state

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



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

$$\hat{T} \equiv -\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i} = -\frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right)$$

⟶ *universal* kinetic energy operator

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

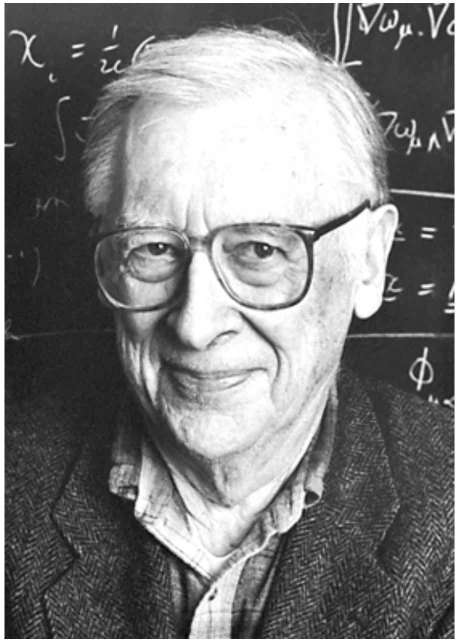
⟶ *universal* two-electron repulsion operator

$$\hat{V} \equiv \sum_{i=1}^{N} v(\mathbf{r}_i)\times \quad \text{where} \quad v(\mathbf{r}) = -\sum_{A}^{\text{nuclei}}\frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}$$

⟶ local *nuclear* potential operator

The Nobel Prize in Chemistry 1998

John Pople - Facts



John A. Pople

Born: 31 October 1925, Burnham-on-Sea, United Kingdom

Died: 15 March 2004, Chicago, IL, USA

Affiliation at the time of the award: Northwestern University, Evanston, IL, USA

Prize motivation: "for his development of computational methods in quantum chemistry"

Field: theoretical chemistry

Prize share: 1/2

(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*.

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

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

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

(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 $\left\langle \Phi_0 \middle| \hat{W}_{\rm ee} \middle| \Phi_0 \right\rangle$ 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 *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: $n_{\Phi_0}(\mathbf{r}) = \sum_{\sigma=\pm\frac{1}{2}} \sum_{i=1}^{N} |\varphi_i(\mathbf{r},\sigma)|^2$
- Electron density for an *interacting* system:

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

Mapping the interacting problem onto a non-interacting one

- There is of course no reason to believe that these two densities are equal.

- However, we may assume that it is possible to *adjust* the local potential in the non-interacting system *such that the two densities become equal*.

- This “magical" potential is known as the *Kohn–Sham* (KS) potential.

- **In summary**:

$$\begin{array}{rcl}\text{interacting problem} & \rightarrow & \textit{non-interacting}\text{ KS problem}\\ \hat{W}_{\text{ee}} & \rightarrow & 0\\ v(\mathbf{r}) & \rightarrow & v^{\text{KS}}(\mathbf{r})\\ n_{\Psi_0}(\mathbf{r}) & = & n_{\Phi_0^{\text{KS}}}(\mathbf{r})\end{array}$$

- Questions to be answered:

(1) If $v^{\text{KS}}(\mathbf{r})$ exists, is it unique? *yes!*

(2) Does the knowledge of $n_{\Psi_0}(\mathbf{r})$ gives access (in principle) to E_0? *yes!*

Wave function theory

$$\begin{tikzcd}
\hat{H} \arrow[d] & n_0(\mathbf{r}) \arrow[d, phantom, "\parallel"] \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[r] \arrow[d] & N\sum_\sigma \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Psi_0(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2 \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \arrow[d, phantom, "\parallel"] & \\
\int d\mathbf{x}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, \Psi_0^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \times \hat{H} \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) &
\end{tikzcd}$$

Wave function theory ***Density functional theory***

$$\begin{tikzcd}
\hat{H} \arrow[d] & n_0(\mathbf{r}) \arrow[l, "\text{Hohenberg-Kohn theorem}"'] \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[d] & \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle &
\end{tikzcd}$$

Wave function theory ***Density functional theory***

$$\begin{tikzcd}
\hat{H} \arrow[d] & n_0(\mathbf{r}) \arrow[ddl] \\
\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \arrow[d] & \\
E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle &
\end{tikzcd}$$

Wave function theory

Density functional theory

$$\hat{H}$$

$$\downarrow$$

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

$$\downarrow$$

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

$$\parallel$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\mathrm{KS}}\right] \longleftarrow N \sum_{\sigma} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\mathrm{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

Kohn-Sham DFT

Wave function theory

Density functional theory

$$\hat{H}$$

$$\big\downarrow$$

$$\Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

$$\big\downarrow$$

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

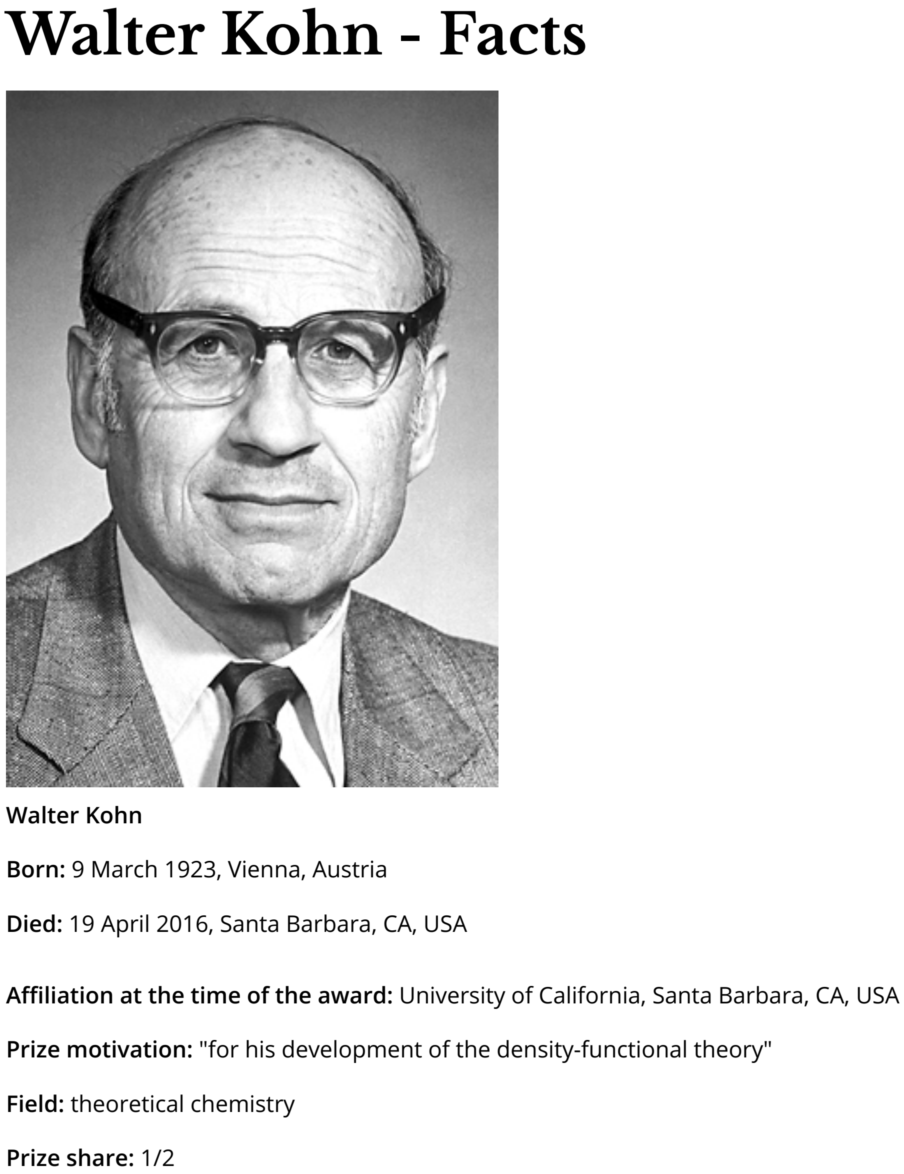
$$\|$$

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\mathrm{KS}}\right] \longleftarrow N \sum_{\sigma} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\mathrm{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

Note that $E_0 \neq \langle \Phi_0^{\mathrm{KS}} | \hat{H} | \Phi_0^{\mathrm{KS}} \rangle$!

Kohn-Sham DFT

The Nobel Prize in Chemistry 1998



Walter Kohn - Facts

Walter Kohn

Born: 9 March 1923, Vienna, Austria

Died: 19 April 2016, Santa Barbara, CA, USA

Affiliation at the time of the award: University of California, Santa Barbara, CA, USA

Prize motivation: "for his development of the density-functional theory"

Field: theoretical chemistry

Prize share: 1/2

Two things to *remember* before we start ...

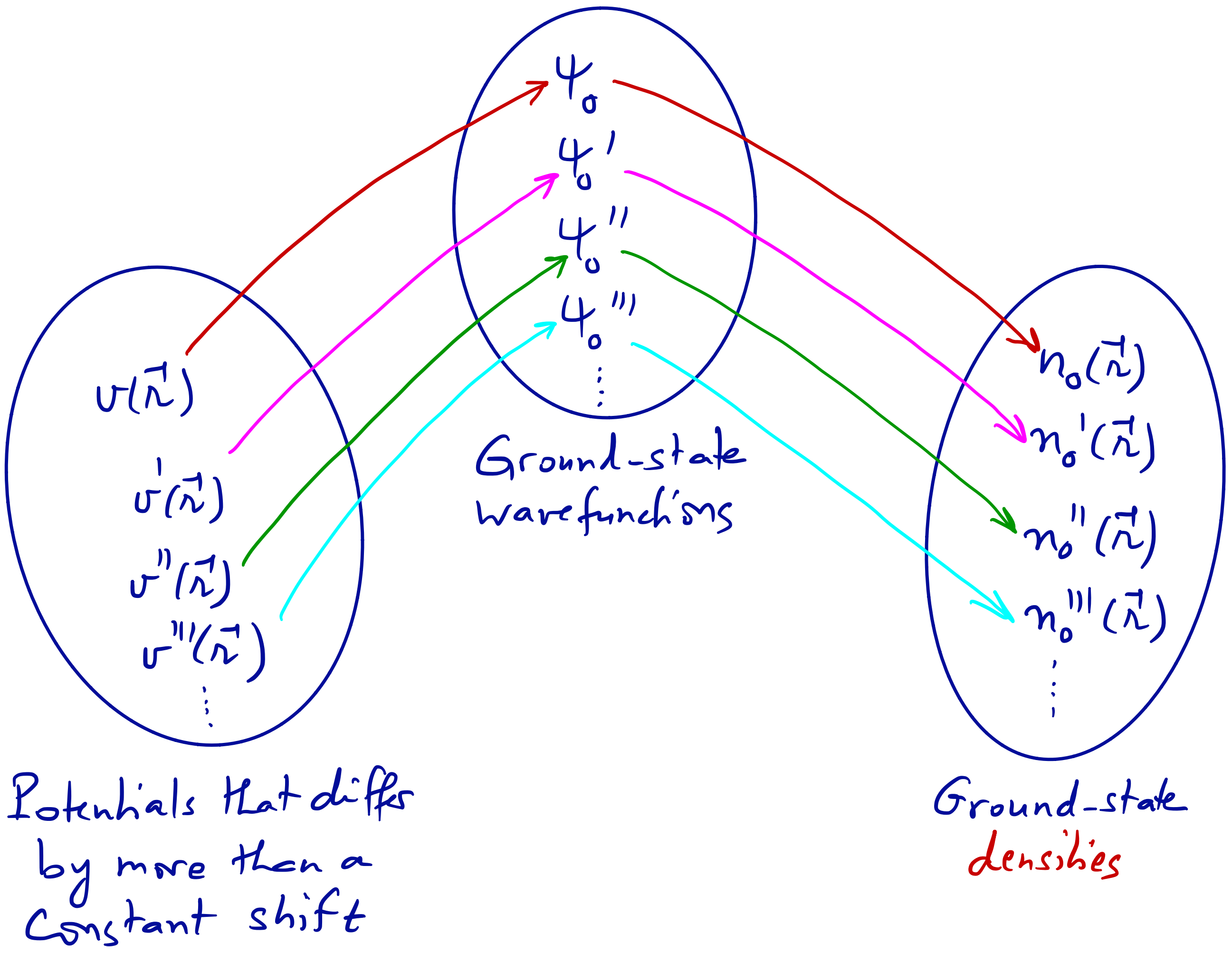
- The following expression for the expectation value of the *one-electron potential energy* in terms of the electron density will be used intensively in the rest of this lecture:

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

- Note that a *constant* shift $v(\mathbf{r}) \rightarrow v(\mathbf{r}) - \mu$ in the local potential does *not* affect the ground-state wavefunction (and therefore it does not affect the ground-state density):

$$\left(\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} \left(v(\mathbf{r}_i) - \mu \right) \times \right) \Psi_0 = \left(\hat{H} \Psi_0 \right) - N\mu \times \Psi_0 = \left(E_0 - N\mu \right) \Psi_0 .$$

First Hohenberg–Kohn theorem



First Hohenberg–Kohn theorem

- Note that $v \rightarrow \Psi_0 \rightarrow E_0$

  $\rightarrow n_0 = n_{\Psi_0}$

- **HK1:** Hohenberg and Kohn* have shown that, in fact, the ground-state electron density fully determines (up to a constant) the local potential v. Therefore

$$n_0 \rightarrow v \rightarrow \Psi_0 \rightarrow E_0$$

- In other words, the ground-state energy is a *functional* of the ground-state density: $E_0 = E[n_0]$.

Proof (part 1):

Let us consider two potentials v and v' that differ by more than a constant, which means that $v(\mathbf{r}) - v'(\mathbf{r})$ varies with $\mathbf{r}$. In the following, we denote Ψ_0 and Ψ'_0 the associated ground-state wavefunctions with energies E_0 and E'_0, respectively.

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

First Hohenberg–Kohn theorem

If $\Psi_0 = \Psi'_0$ then

$$\begin{aligned}
\sum_{i=1}^{N} \Big(v(\mathbf{r}_i) - v'(\mathbf{r}_i) \Big) \times \Psi_0 &= \sum_{i=1}^{N} v(\mathbf{r}_i) \times \Psi_0 - v'(\mathbf{r}_i) \times \Psi'_0 \\
&= \left(\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \right) \Psi_0 - \left(\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v'(\mathbf{r}_i) \times \right) \Psi'_0 \\
&= E_0 \Psi_0 - E'_0 \Psi'_0 \\
&= \big(E_0 - E'_0 \big) \times \Psi_0
\end{aligned}$$

so that, in the particular case $\mathbf{r}_1 = \mathbf{r}_2 = \ldots = \mathbf{r}_N = \mathbf{r}$, we obtain

$$v(\mathbf{r}) - v'(\mathbf{r}) = \big(E_0 - E'_0 \big)/N \qquad \longrightarrow \qquad \text{constant (absurd!)}$$

Therefore Ψ_0 and Ψ'_0 cannot be equal.

First Hohenberg–Kohn theorem

Proof (part 2): Let us now assume that Ψ_0 and Ψ'_0 have the same electron density n_0.

According to the Rayleigh–Ritz variational principle

$$E_0 < \underbrace{\left\langle \Psi'_0 \middle| \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times \middle| \Psi'_0 \right\rangle}_{E'_0 + (v - v'|n_0)} \quad \text{and} \quad E'_0 < \underbrace{\left\langle \Psi_0 \middle| \hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^{N} v'(\mathbf{r}_i) \times \middle| \Psi_0 \right\rangle}_{E_0 - (v - v'|n_0)}$$

thus leading to

$$0 < E_0 - E'_0 - (v - v'|n_0) < 0 \qquad \text{absurd!}$$

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

Second Hohenberg–Kohn theorem

HK2: The exact ground-state density $n_0(\mathbf{r})$ of the electronic Hamiltonian

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

minimizes the energy density functional $E[n] = F[n] + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\rm ne}(\mathbf{r})n(\mathbf{r}),$

where the Hohenberg–Kohn universal functional $F[n]$ is defined as

$$F[n] = \langle \Psi[n]|\hat{T} + \hat{W}_{\rm ee}|\Psi[n]\rangle,$$

and the minimum equals the exact ground-state energy E_0:

$$\boxed{\min_n E[n] = E[n_0] = E_0}$$

Comment: we know from **HK1** that $n(\mathbf{r}) \;\rightarrow\; v[n](\mathbf{r}) \;\rightarrow\; \underbrace{\Psi[v[n]] = \Psi[n]}$

ground-state wavefunction with density n.

Second Hohenberg–Kohn theorem

Proof:

- for any density $n(\mathbf{r})$, $\Psi[n]$ is well defined according to **HK1** and

$$\langle \Psi[n] | \hat{H}[v_{\text{ne}}] | \Psi[n] \rangle \geq E_0$$

$$\underbrace{\langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle}_{F[n]} + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\text{ne}}(\mathbf{r})\, \underbrace{n_{\Psi[n]}(\mathbf{r})}_{n(\mathbf{r})} \geq E_0$$

thus leading to $\boxed{E[n] \geq E_0}$

- When $n(\mathbf{r})$ equals the exact ground-state density $n_0(\mathbf{r})$:

$$n_0(\mathbf{r}) \quad \rightarrow \quad v_{\text{ne}}(\mathbf{r}) \quad \rightarrow \quad \Psi[n_0] = \Psi[v_{\text{ne}}] = \Psi_0$$

$$E[n_0] = \langle \Psi_0 | \hat{T} + \hat{W}_{\text{ee}} | \Psi_0 \rangle + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\text{ne}}(\mathbf{r}) n_0(\mathbf{r}) = \langle \Psi_0 | \hat{T} + \hat{W}_{\text{ee}} + \hat{V}_{\text{ne}} | \Psi_0 \rangle = E_0$$

Kohn–Sham DFT (KS-DFT)

- The HK theorems apply to non-interacting electrons:

$$
\begin{array}{rcl}
\text{interacting problem} & \rightarrow & \textit{non-interacting}\ \text{KS problem} \\[2em]
\hat{W}_{\rm ee} & \rightarrow & 0 \\
v[n](\mathbf{r}) & \rightarrow & v^{\rm KS}[n](\mathbf{r}) \\
\Psi[n] & \rightarrow & \Phi^{\rm KS}[n] \\
F[n] & \rightarrow & T_{\rm s}[n] = \left\langle \Phi^{\rm KS}[n] \middle| \hat{T} \middle| \Phi^{\rm KS}[n] \right\rangle \\[2em]
n_{\Psi[n]}(\mathbf{r}) & = & n_{\Phi^{\rm KS}[n]}(\mathbf{r}) \ = \ n(\mathbf{r})
\end{array}
$$

- *KS decomposition* of the universal HK functional:

$$
\boxed{F[n] = T_{\rm s}[n] + E_{\rm Hxc}[n]} \qquad \text{with} \qquad E_{\rm Hxc}[n] = \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + E_{\rm xc}[n].
$$

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

How can we determine the KS determinant?

Levy–Lieb constrained search formalism

- For a given density n there is a unique potential $v_{\mathrm{KS}}[n](\mathbf{r})$, if it exists ..., such that $\Phi^{\mathrm{KS}}[n]$ is the ground state of $\hat{T} + \sum_{i=1}^{N} v_{\mathrm{KS}}[n](\mathbf{r}_i)\times$ with density n.

- For all normalized wavefunctions Ψ with density n the following inequality is fulfilled:

$$\left\langle \Phi^{\mathrm{KS}}[n] \middle| \left(\hat{T} + \sum_{i=1}^{N} v_{\mathrm{KS}}[n](\mathbf{r}_i)\times \right) \middle| \Phi^{\mathrm{KS}}[n] \right\rangle \leq \left\langle \Psi \middle| \left(\hat{T} + \sum_{i=1}^{N} v_{\mathrm{KS}}[n](\mathbf{r}_i)\times \right) \middle| \Psi \right\rangle$$

$$\longrightarrow \quad T_{\mathrm{s}}[n] \leq \langle \Psi|\hat{T}|\Psi\rangle \quad \longrightarrow \quad \boxed{T_{\mathrm{s}}[n] = \min_{\Psi \rightarrow n} \langle \Psi|\hat{T}|\Psi\rangle}$$

- Therefore $\langle \Phi^{\mathrm{KS}}|\hat{T}|\Phi^{\mathrm{KS}}\rangle = T_{\mathrm{s}}[n_0] = \min_{\Psi \rightarrow n_0} \langle \Psi|\hat{T}|\Psi\rangle$ but we do not know n_0 ...

- Note that, as a consequence of the previous equality, $T_{\mathrm{s}}[n_0] \leq \langle \Psi_0|\hat{T}|\Psi_0\rangle$!

Kohn–Sham DFT (KS-DFT)

- For any normalized wavefunction Ψ,

$$\begin{aligned}
\langle\Psi|\hat{T}|\Psi\rangle &\geq T_{\mathrm{s}}[n_\Psi] \\
\langle\Psi|\hat{T}+\hat{V}_{\mathrm{ne}}|\Psi\rangle &\geq T_{\mathrm{s}}[n_\Psi] + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\mathrm{ne}}(\mathbf{r}) n_\Psi(\mathbf{r}) \\
\langle\Psi|\hat{T}+\hat{V}_{\mathrm{ne}}|\Psi\rangle + E_{\mathrm{Hxc}}[n_\Psi] &\geq \underbrace{T_s[n_\Psi] + E_{\mathrm{Hxc}}[n_\Psi] + \int_{\mathbb{R}^3} d\mathbf{r}\; v_{\mathrm{ne}}(\mathbf{r}) n_\Psi(\mathbf{r})}_{E[n_\Psi]\geq E_0}
\end{aligned}$$

- The exact ground-state energy E_0 is recovered when $\Psi = \Phi^{\mathrm{KS}}$ thus leading to

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

- Note that the minimization can be restricted to single determinantal wavefunctions Φ.

Comparing wave function theory (WFT) with KS-DFT

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

$\downarrow$ WFT

$\downarrow$ DFT

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

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

Standard density-functional approximations (DFAs)

Local and semi-local functionals

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

LDA *(uniform electron gas)*

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

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

⋮

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)*

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

B3LYP

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

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

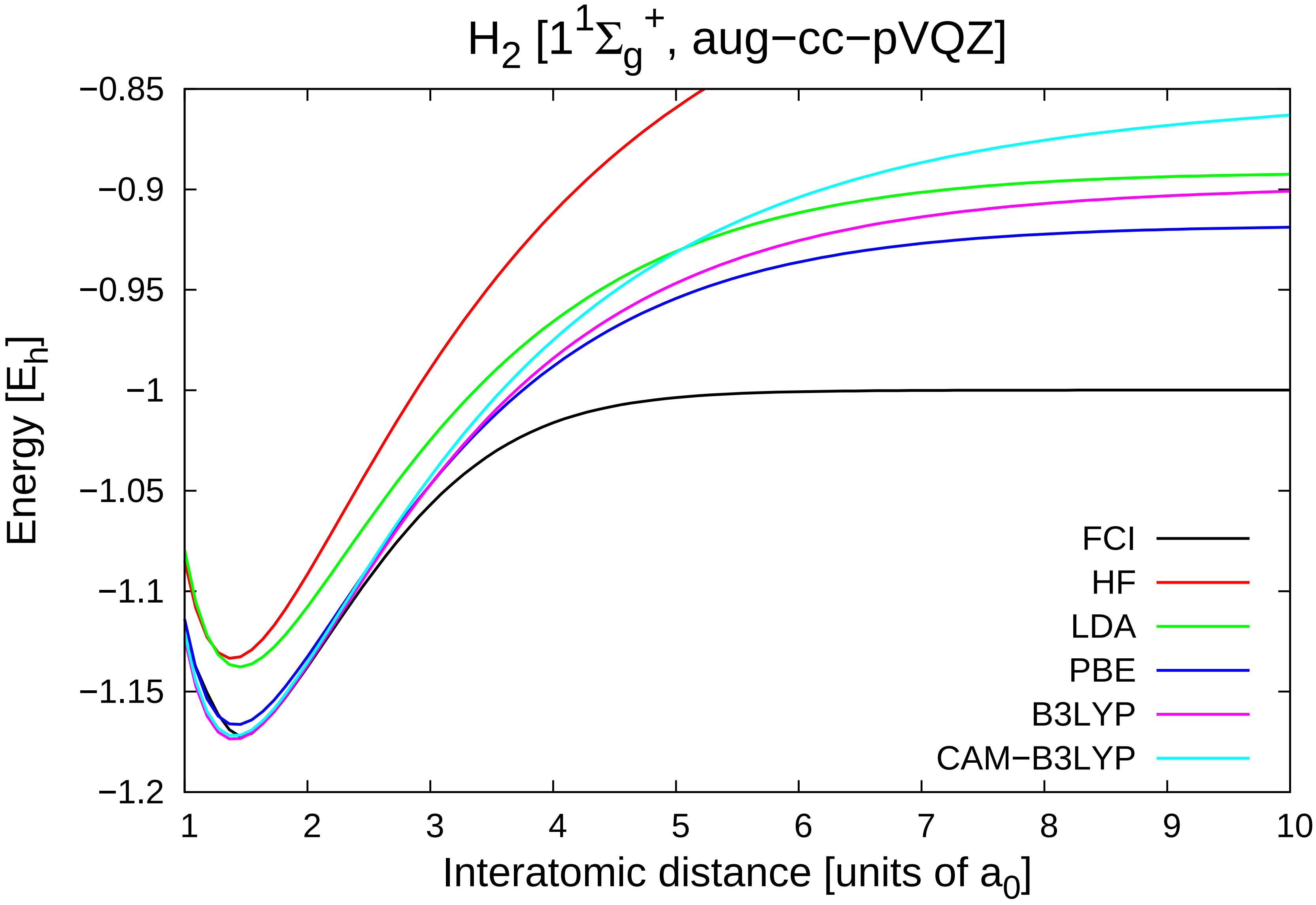
⋮

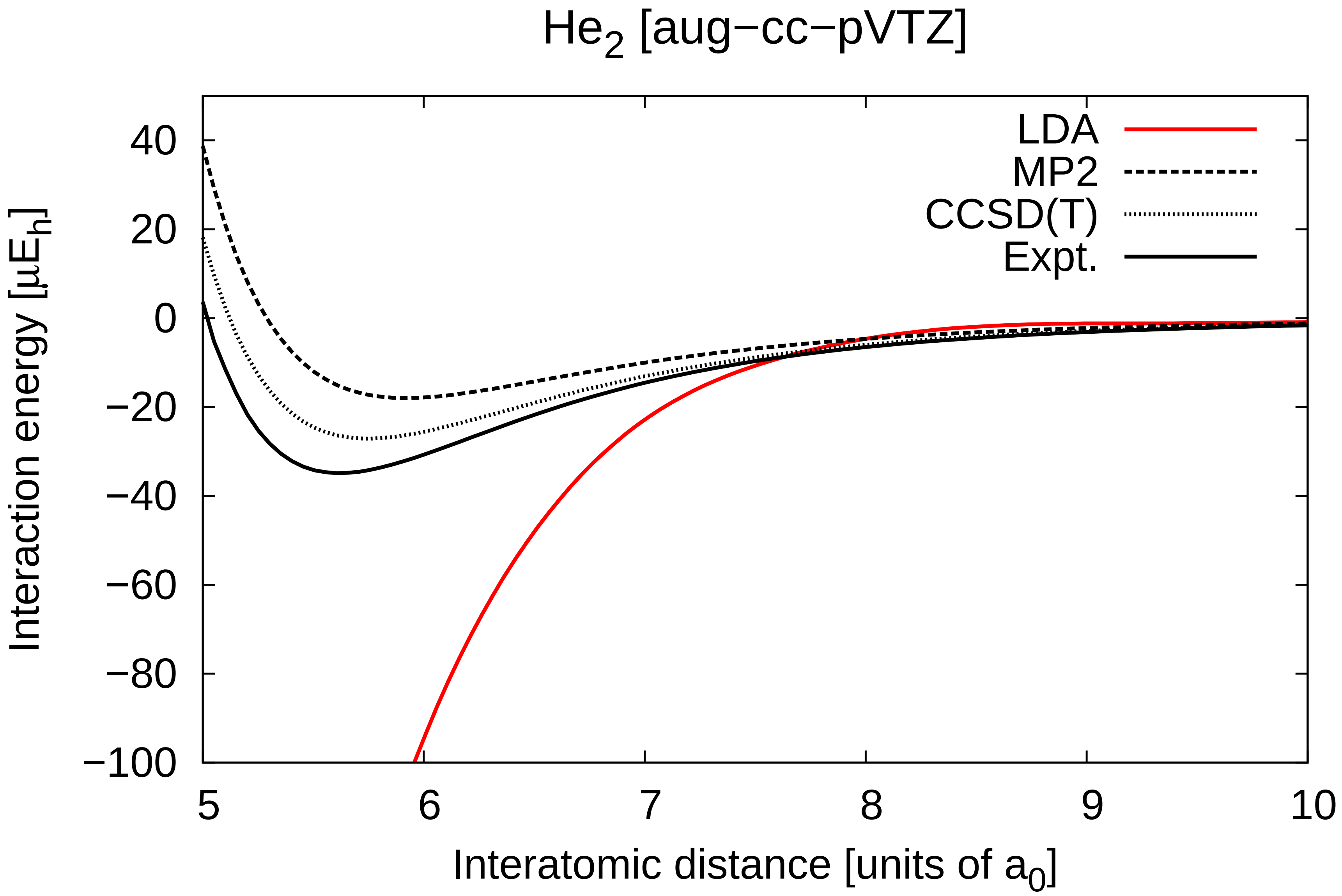
$$\hat{W}_{\mathrm{ee}} = \underbrace{\hat{W}_{\mathrm{ee}}^{\mathrm{lr}}}_{\text{Long-range}} + \underbrace{\hat{W}_{\mathrm{ee}}^{\mathrm{sr}}}_{\text{short-range}}$$

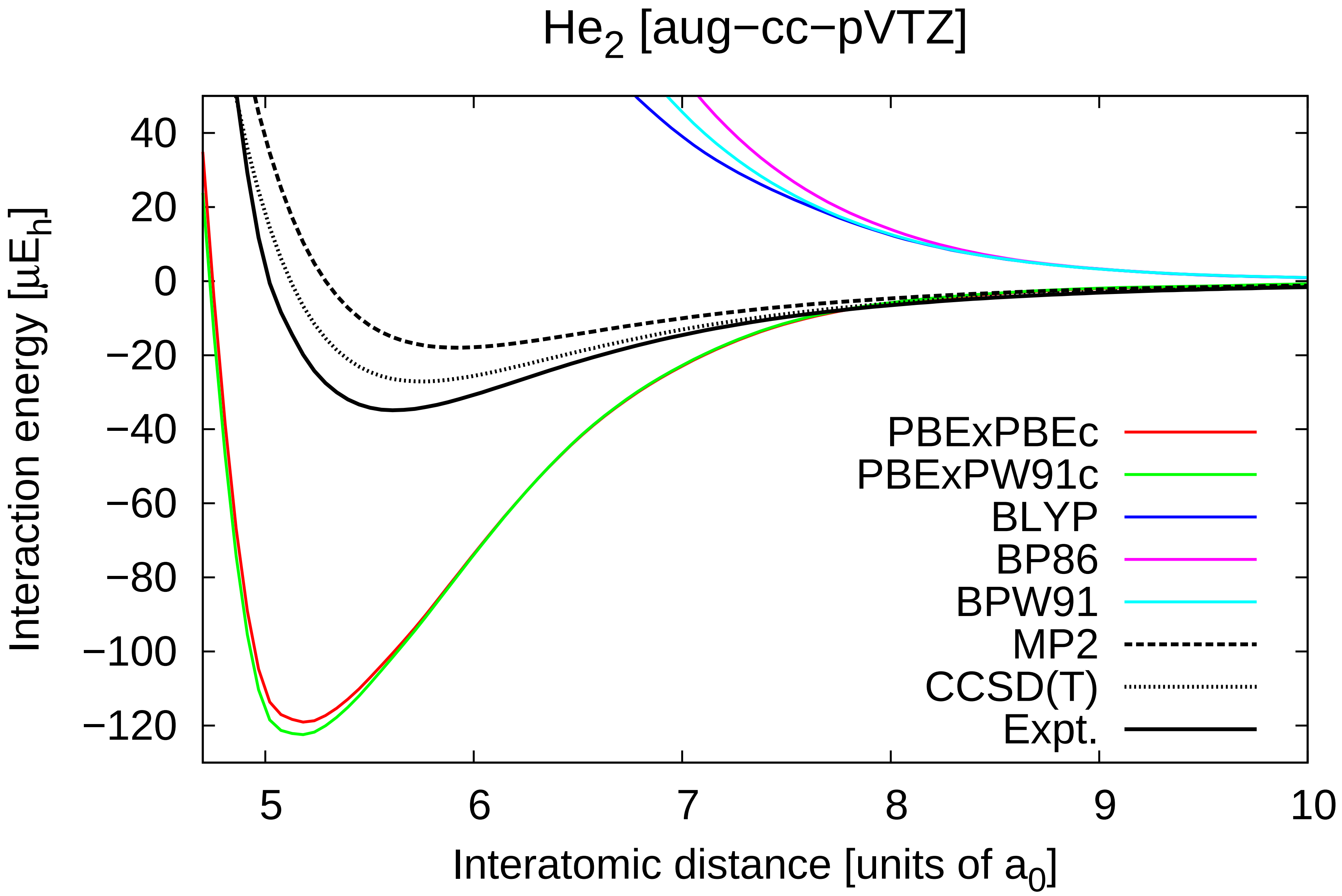
Range-separated hybrids

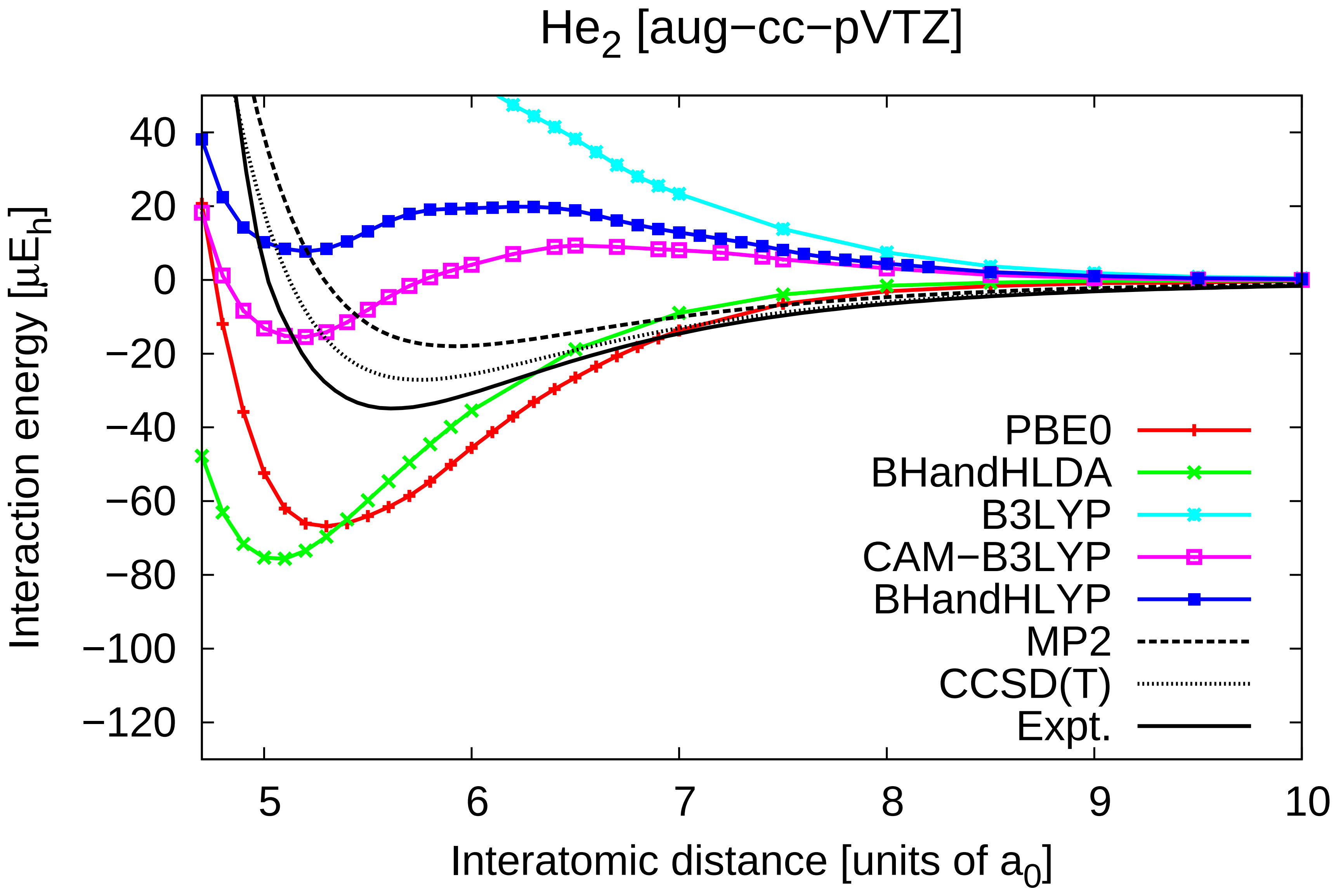
CAM-B3LYP

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

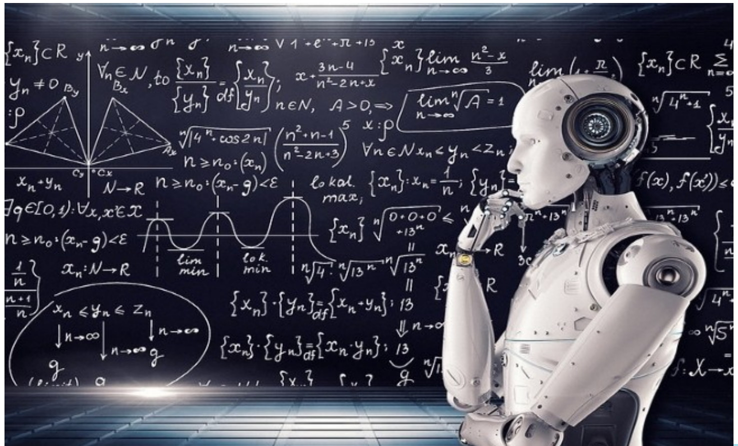

H$_2$ [$1^1\Sigma_g^+$, aug−cc−pVQZ]
Energy [E$_h$]
−0.85
−0.9
−0.95
−1
−1.05
−1.1
−1.15
−1.2
1
2
3
4
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
FCI
HF
LDA
PBE
B3LYP
CAM−B3LYP


He_2 [aug−cc−pVTZ]
LDA
MP2
CCSD(T)
Expt.
Interaction energy [μE_h]
40
20
0
−20
−40
−60
−80
−100
5
6
7
8
9
10
Interatomic distance [units of a_0]


He₂ [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 a₀]
PBExPBEc
PBExPW91c
BLYP
BP86
BPW91
MP2
CCSD(T)
Expt.

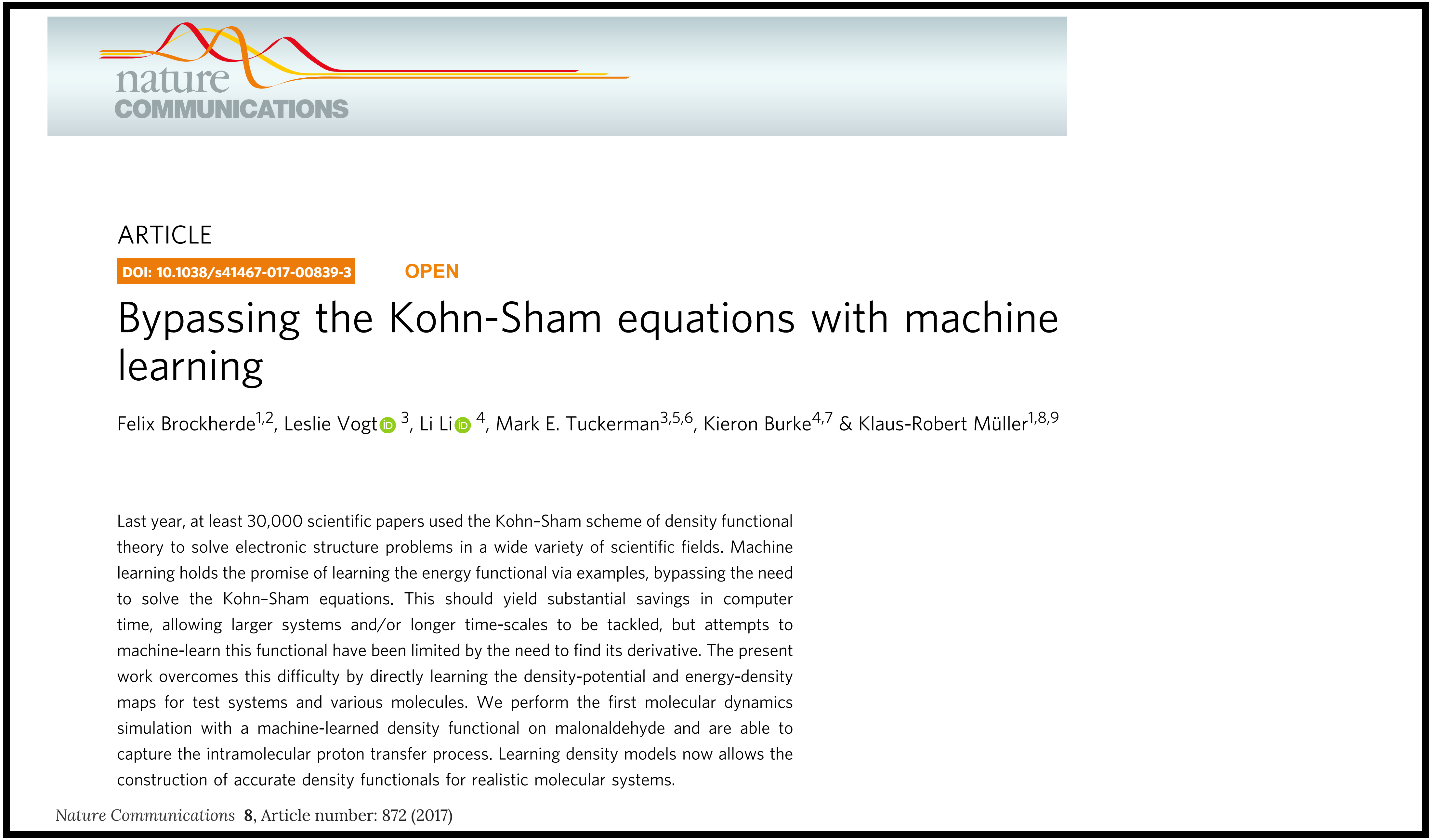

He$_2$ [aug−cc−pVTZ]
Interaction energy [μE$_h$]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
PBE0
BHandHLDA
B3LYP
CAM−B3LYP
BHandHLYP
MP2
CCSD(T)
Expt.

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_0 variationally from $v_{\rm ne}$.
- What about *learning the map* $v \rightarrow n[v]$ directly ?*
- If we have $v_{\rm ne}$, the machine will tell us directly what the ground-state density $n_0 = n[v_{\rm ne}]$ is.
- We can also *teach* the machine how to *compute the energy* $E[n_0] = T_{\rm s}[n_0] + E_{\rm Hxc}[n_0] + (v_{\rm ne}|n_0)$.

* 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 $\{\phi_l(\mathbf{r})\}_{1\leq l\leq L}$:

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

- 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.

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Teaching the HK theorem to a machine

- The machine will learn

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

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

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

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

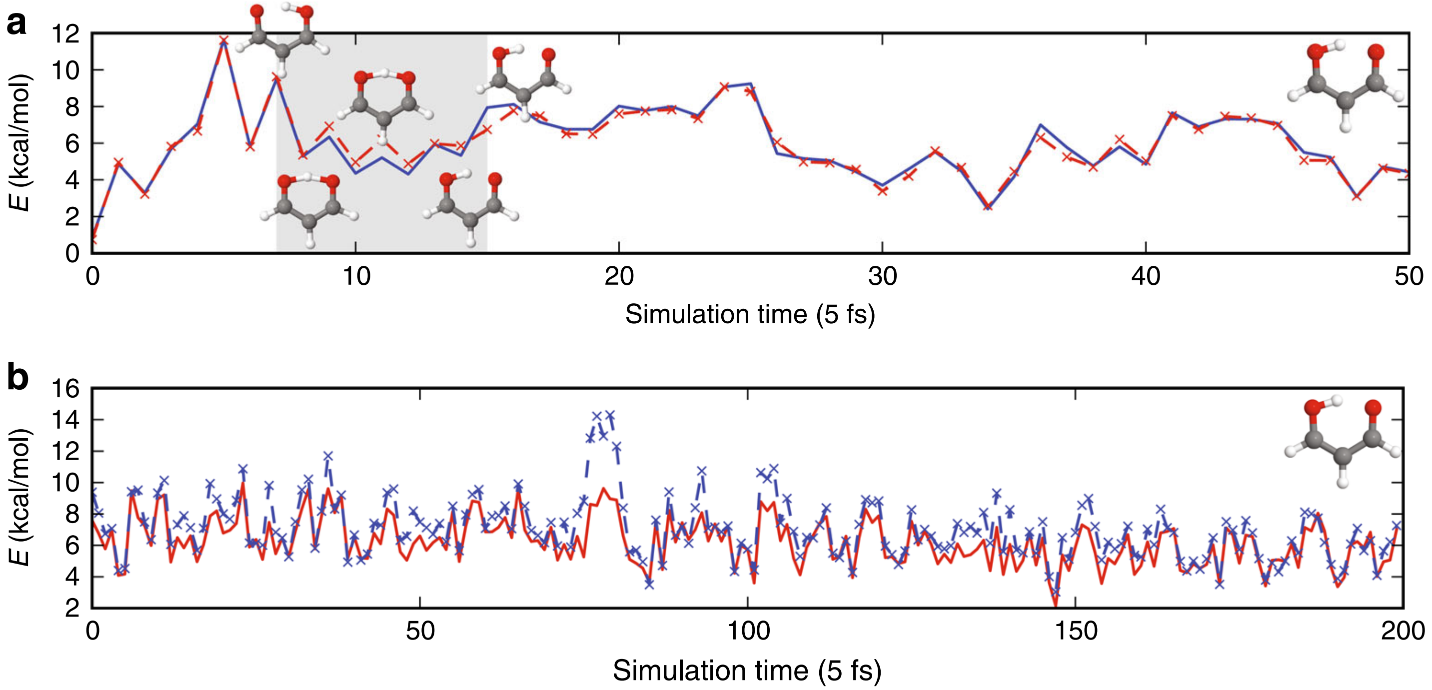

Fig. 5 Energy errors of ML-HK along ab initio MD and ML-generated trajectories. **a** Energy errors of ML-HK along a 0.25 ps ab initio MD trajectory of malonaldehyde. PBE values in *blue*, ML-HK values in *red*. The ML model correctly predicts energies during proton transfer in frames 7–15 without explicit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