Introduction to Kohn–Sham density-functional theory

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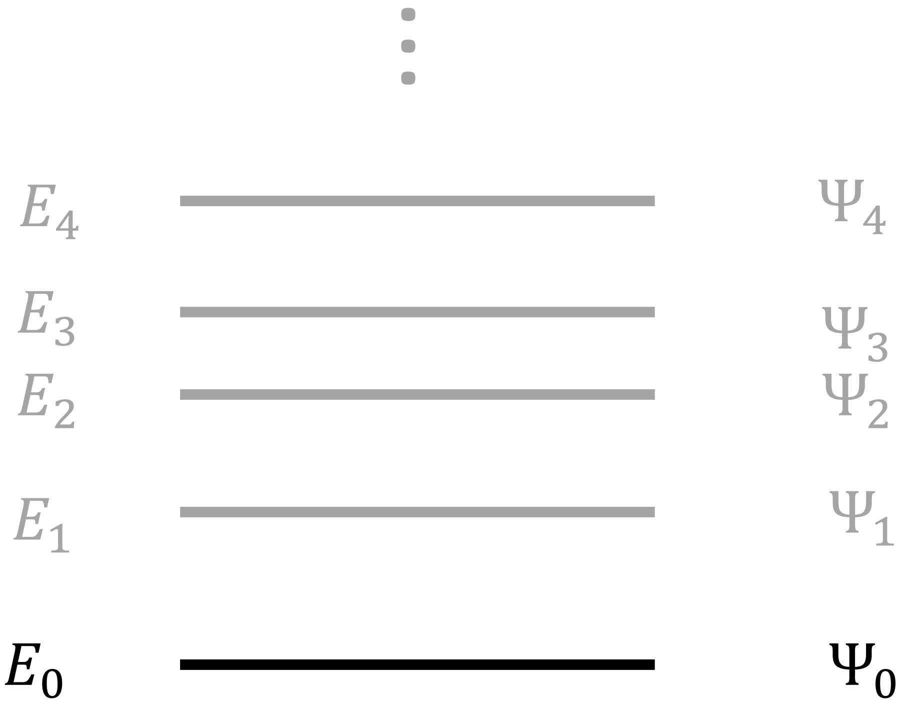
Schrödinger equation for the *ground* state



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

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

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

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

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

- Φ_0 should be *antisymmetrized* with respect to any permutation $\mathbf{x}_i \leftrightarrow \mathbf{x}_j$ (otherwise it is *not* physical):

$$\Phi_0(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_N) = -\Phi_0(\mathbf{x}_1, \ldots, \mathbf{x}_j, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N).$$

- Non-interacting electrons are described exactly with a single *Slater determinant* Φ_0 (instead of a Hartree product).

- 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).

- The energy contribution that is missing is referred to as *correlation* energy.

(Real) interacting many-electron problem

- Describing interacting electrons ($\hat{W}_{\rm ee} \neq 0$) is *not* straightforward. Indeed, the exact two-electron solution $\Psi_0(\mathbf{r}_1, \mathbf{r}_2)$ to the interacting Schrödinger equation cannot be written as $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$:

$$\boxed{\Psi_0(\mathbf{r}_1, \mathbf{r}_2) \neq \varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2).}$$

Proof : Let us assume that we can find an orbital $\varphi(\mathbf{r})$ such that $\hat{H}\Big(\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\Big) = E_0\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ for any $\mathbf{r}_1$ and $\mathbf{r}_2$ values. Consequently,

$$\hat{W}_{\rm ee}\Big(\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\Big) = E_0\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) - \Big(\hat{T} + \hat{V}\Big)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2).$$

Using the definition of the operators and dividing by $\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)$ leads to

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = E_0 + \frac{1}{2}\frac{\nabla^2_{\mathbf{r}_1}\varphi(\mathbf{r}_1)}{\varphi(\mathbf{r}_1)} + \frac{1}{2}\frac{\nabla^2_{\mathbf{r}_2}\varphi(\mathbf{r}_2)}{\varphi(\mathbf{r}_2)} - v(\mathbf{r}_1) - v(\mathbf{r}_2).$$

In the limit $\mathbf{r}_2 \rightarrow \mathbf{r}_1 = \mathbf{r}$, it comes $\forall\, \mathbf{r}, \quad E_0 + \dfrac{\nabla^2_{\mathbf{r}}\varphi(\mathbf{r})}{\varphi(\mathbf{r})} - 2v(\mathbf{r}) \rightarrow +\infty$ absurd!

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:

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

- Note that $\int d\mathbf{r}\, n_{\Phi_0}(\mathbf{r}) = \int d\mathbf{r}\, n_{\Psi_0}(\mathbf{r}) = N$ ←*number of electrons!*

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**:

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

- Questions to be answered:

(1) If $v^{\rm KS}(\mathbf{r})$ 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

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

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

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

Wave function theory

Density functional theory

$$\hat{H}$$

$$\downarrow$$

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

$$\downarrow$$

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

$$\|$$

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

Kohn-Sham DFT

Wave function theory

Density functional theory

$$\hat{H}$$

$$\downarrow$$

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

$$\downarrow$$

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

$$\parallel$$

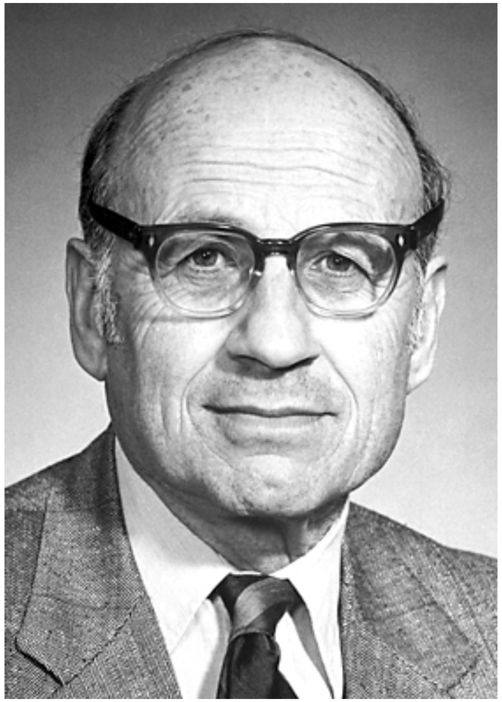
$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle = E\left[\Phi_0^{\mathrm{KS}}\right] \longleftarrow N \sum_{\sigma} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \, |\Phi_0^{\mathrm{KS}}(\mathbf{r}, \sigma, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2$$

Kohn-Sham DFT

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

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

Three 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):

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

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

- **Rayleigh–Ritz variational principle**: the exact ground-state energy is a lower bound for the expectation value of the energy. The minimum is reached when the trial quantum state $|\Psi\rangle$ equals the ground state $|\Psi_0\rangle$:

$$E_0 = \min_{\Psi} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\langle\Psi_0|\hat{H}|\Psi_0\rangle}{\langle\Psi_0|\Psi_0\rangle}.$$

Proof: $\forall\,\Psi,\ |\Psi\rangle = \sum_{I\geq 0} C_I|\Psi_I\rangle$ and $\langle\Psi|\hat{H}|\Psi\rangle - E_0\langle\Psi|\Psi\rangle = \sum_{I>0} |C_I|^2\Big(E_I - E_0\Big) \geq 0.$

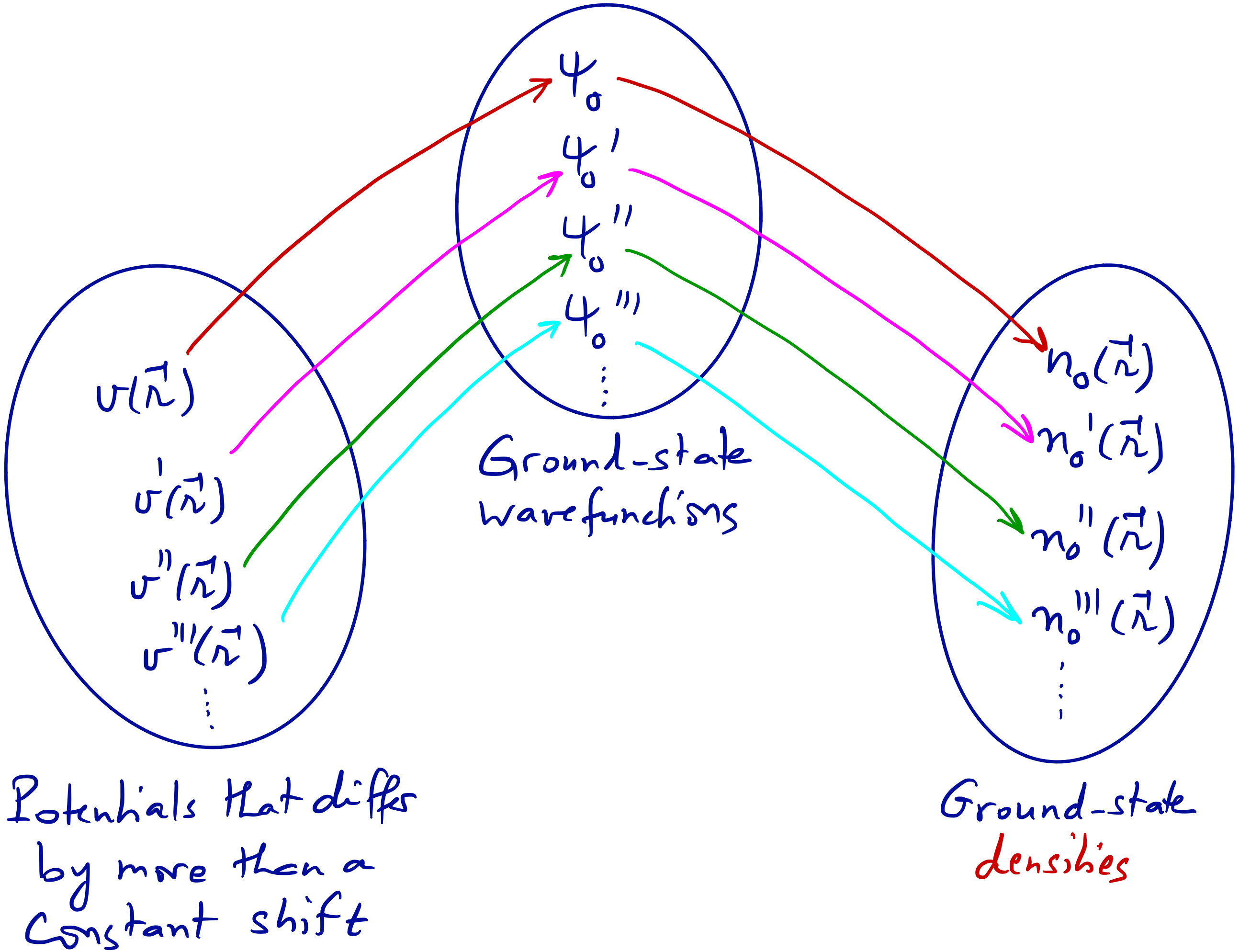
- The ground state is usually normalized $\Big(\langle\Psi_0|\Psi_0\rangle = 1\Big)$ so that the variational principle can be rewritten as follows,

$$\boxed{E_0 = \min_{\Psi,\langle\Psi|\Psi\rangle=1} \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_0|\hat{H}|\Psi_0\rangle}$$

- Comment: If $|\Psi_0\rangle$ is not degenerate, any normalized state $|\Psi\rangle$ that is not equal to $|\Psi_0\rangle$ is such that $\langle\Psi|\hat{H}|\Psi\rangle > E_0$.

Potential-density maps

Interacting map: $\hat{H} \equiv \hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$ or *Non-interacting (KS) map:* $\hat{H} \equiv \hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$



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

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

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

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

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

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

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 and Kohn theorem

Proof:

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

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

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

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

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

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

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

Kohn–Sham DFT (KS-DFT)

- The HK theorems apply to non-interacting electrons:

interacting problem → *non-interacting* KS problem

$$\begin{aligned} \hat{W}_{\rm ee} &\rightarrow 0 \\ v[n](\mathbf{r}) &\rightarrow v^{\rm KS}[n](\mathbf{r}) \\ \Psi[n] &\rightarrow \Phi^{\rm KS}[n] \\ F[n] &\rightarrow T_{\rm s}[n] = \left\langle \Phi^{\rm KS}[n] \middle| \hat{T} \middle| \Phi^{\rm KS}[n] \right\rangle \end{aligned}$$

$$n_{\Psi[n]}(\mathbf{r}) = n_{\Phi^{\rm KS}[n]}(\mathbf{r}) = n(\mathbf{r})$$

- *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 potential?

Two mathematical interludes

Mathematical interlude 1: functional derivative

- Let $f : x \longmapsto f(x)$ be a function of x. The derivative of f at $x = x_0$ is obtained from the Taylor expansion [δx is a small variation of x around x_0]

$$f(x_0 + \delta x) = f(x_0) + \delta x \left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x=x_0} + \frac{(\delta x)^2}{2} \left.\frac{\mathrm{d}^2 f(x)}{\mathrm{d}x^2}\right|_{x=x_0} + \ldots$$

- Let $S : n \longmapsto S[n]$ be a functional of the density n. The *functional derivative* of S at $n = n_0$ is by definition a *function of* $\mathbf{r}$ that is denoted $\boxed{\dfrac{\delta S[n_0]}{\delta n(\mathbf{r})} \equiv \left.\dfrac{\delta S[n]}{\delta n(\mathbf{r})}\right|_{n=n_0}}$. The latter is obtained from the following Taylor expansion [$\delta n(\mathbf{r})$ is a small deviation from $n_0(\mathbf{r})$ of the density at the position $\mathbf{r}$]:

$$S[n_0 + \delta n] = S[n_0] + \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, \frac{\delta S[n_0]}{\delta n(\mathbf{r})} \times \delta n(\mathbf{r}) + \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \, \frac{\delta^2 S[n_0]}{\delta n(\mathbf{r})\delta n(\mathbf{r}')} \times \delta n(\mathbf{r})\delta n(\mathbf{r}') + \ldots$$

- Example: $S[n] = \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}\, n^2(\mathbf{r}) \quad \longrightarrow \quad \dfrac{\delta S[n_0]}{\delta n(\mathbf{r})} = 2n_0(\mathbf{r})$

Mathematical interlude 2: Lieb maximization

- Let $E[v]$ be the ground-state energy of $\hat{T}+\hat{W}_{\rm ee}+\sum_{i=1}^{N} v(\mathbf{r}_i)\times$
- According to the second (variational) HK theorem:

$$\boxed{\forall v,\quad E[v]=\min_{n}\left\{F[n]+\int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})\right\}} \quad\Leftrightarrow\quad \forall v,\forall n,\quad E[v]\leq F[n]+\int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$$

$$\Leftrightarrow\quad \forall v,\forall n,\quad F[n]\geq E[v]-\int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})$$

$$\Leftrightarrow\quad \boxed{\forall n,\quad F[n]=\max_{v}\left\{E[v]-\int d\mathbf{r}\, v(\mathbf{r})n(\mathbf{r})\right\}}$$

- Note that the *maximizing potential is* $v[n]$.

E. H . Lieb, Int. J. Quant. Chem. **24**, 243 (1983).

Finding the Kohn–Sham potential

- A *variation* $n \rightarrow n+\delta n$ *in density* induces a variation $v[n] \rightarrow v[n+\delta n] = v[n]+\delta v[n]$ in potential:

$$\delta F[n] = F[n+\delta n] - F[n] = \delta\left[\left(E[v] - \int d\mathbf{r}\, v(\mathbf{r}) n(\mathbf{r})\right)_{v=v[n]}\right] \overset{\text{Lieb max.}}{=} - \int d\mathbf{r}\, v[n](\mathbf{r}) \times \delta n(\mathbf{r}) + \ldots$$

- Therefore $\boxed{\dfrac{\delta F[n]}{\delta n(\mathbf{r})} = -v[n](\mathbf{r})}$, which gives, *for non-interacting systems*: $\boxed{\dfrac{\delta T_{\mathrm{s}}[n]}{\delta n(\mathbf{r})} = -v^{\mathrm{KS}}[n](\mathbf{r})}$.

- According to the *first HK theorem*, $v[n_0](\mathbf{r}) = v_{\mathrm{ne}}(\mathbf{r})$, so that

$$\begin{aligned} v^{\mathrm{KS}}[n_0](\mathbf{r}) &= v[n_0](\mathbf{r}) + \left(v^{\mathrm{KS}}[n](\mathbf{r}) - v[n](\mathbf{r})\right)_{n=n_0} \\ &= \boxed{v_{\mathrm{ne}}(\mathbf{r}) + \frac{\delta E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r})} = v^{\mathrm{KS}}[n_0](\mathbf{r})} \end{aligned}$$

Self-consistent KS equations

$$\left(-\frac{1}{2}\nabla^2_{\mathbf{r}} + v_{\rm ne}(\mathbf{r}) + \frac{\delta E_{\rm Hxc}[n_0]}{\delta n(\mathbf{r})}\right)\varphi_i^{\rm KS}(\mathbf{x}) = \varepsilon_i^{\rm KS}\varphi_i^{\rm KS}(\mathbf{x})$$

where $$n_0(\mathbf{r}) = \sum_{\sigma=\pm\frac{1}{2}}\sum_{i=1}^{N}\left|\varphi_i^{\rm KS}(\mathbf{r},\sigma)\right|^2.$$

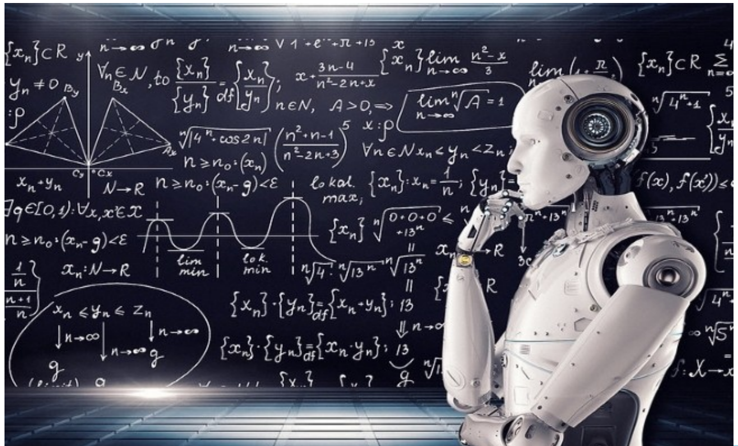
Important conclusion: if we know the *xc functional* $E_{\rm xc}[n]$, we can determine the ground-state density *self-consistently* (and therefore the ground-state energy), in principle *exactly*.

In KS-DFT, the physical ground-state *energy* reads

$$E_0 = T_{\rm s}[n_0] + E_{\rm Hxc}[n_0] + \int_{\mathbb{R}^3} {\rm d}\mathbf{r}\, v_{\rm ne}(\mathbf{r})n_0(\mathbf{r}),$$

where $$T_{\rm s}[n_0] = \left\langle \Phi_0^{\rm KS}\middle|\hat{T}\middle|\Phi_0^{\rm KS}\right\rangle = -\frac{1}{2}\sum_{i=1}^{N}\int {\rm d}\mathbf{x}\,\varphi_i^{\rm KS}(\mathbf{x})\nabla^2_{\mathbf{r}}\varphi_i^{\rm KS}(\mathbf{x}).$$

Developing density-functional approximations (DFAs)



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

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

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**).*

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

$$\vdots$$

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**).*

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

$$\vdots$$

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

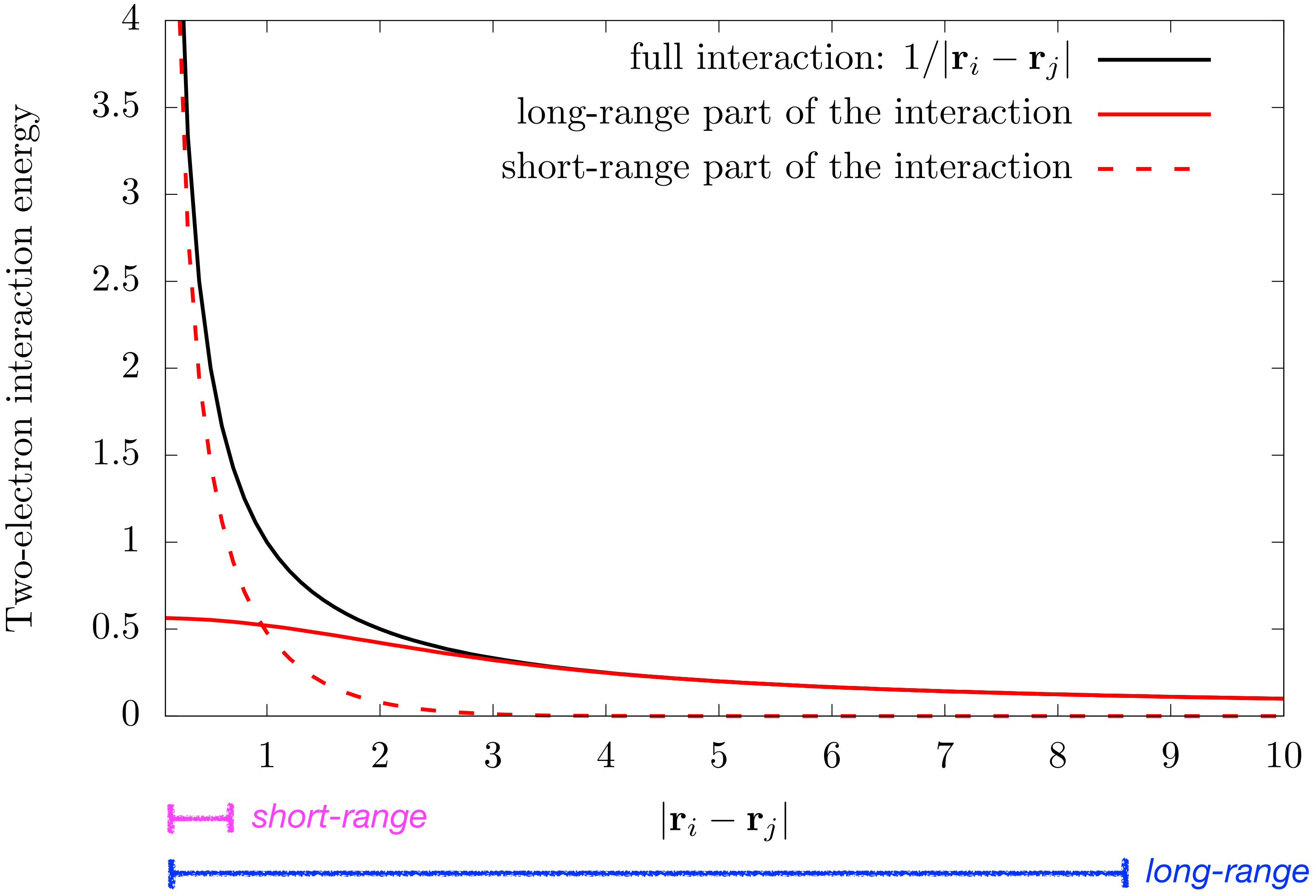
Long-range short-range

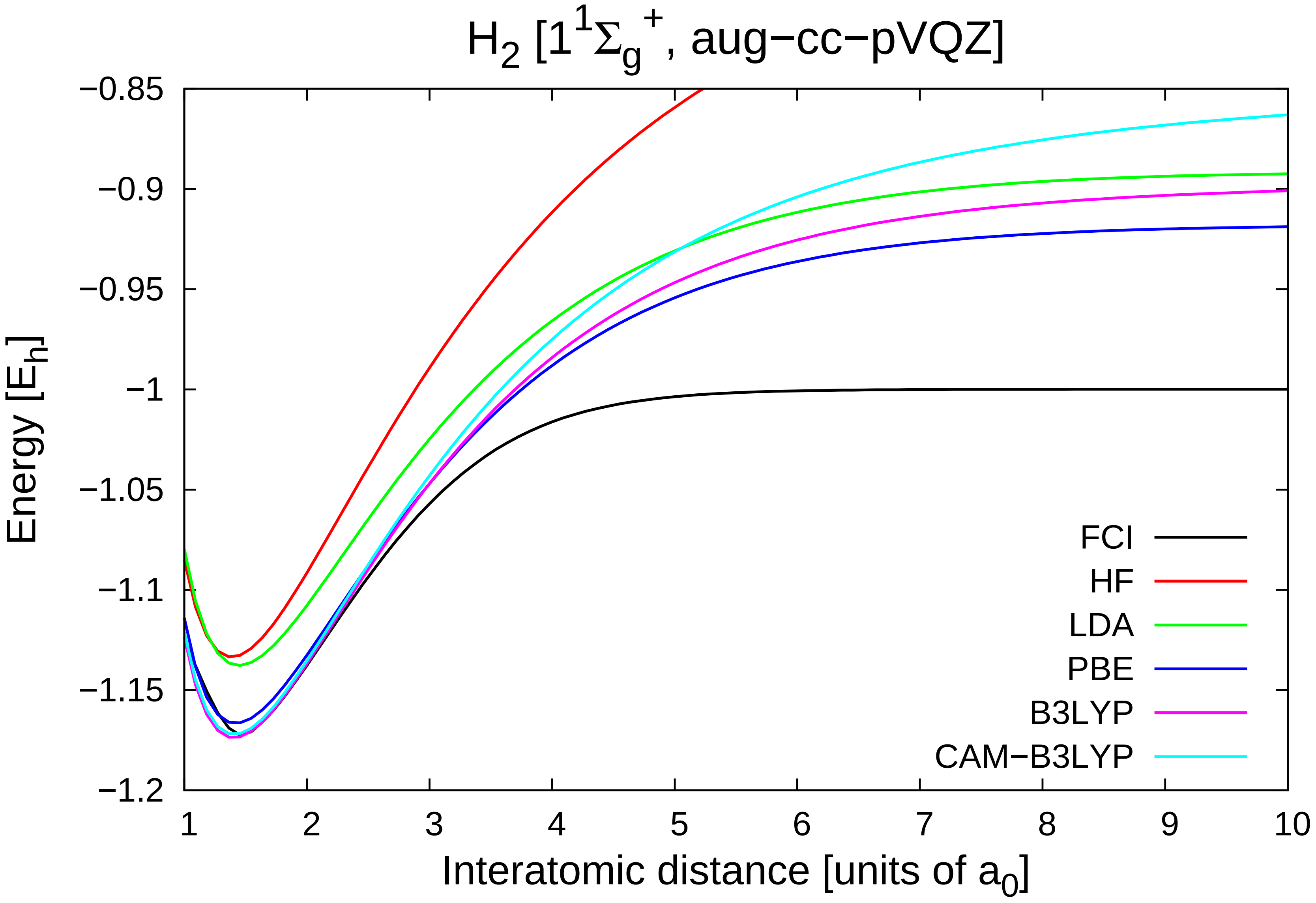
Range-separated hybrids

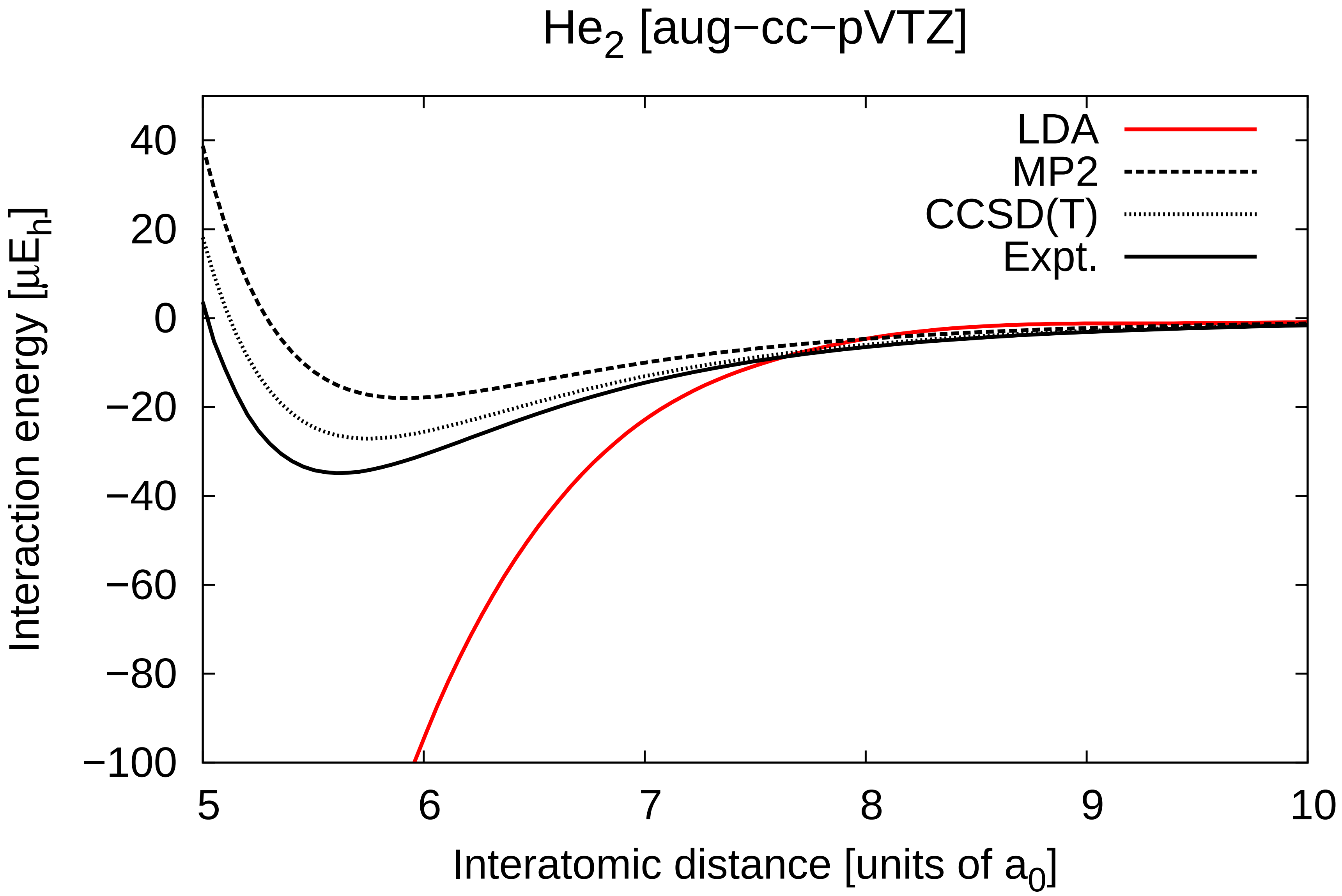
CAM-B3LYP

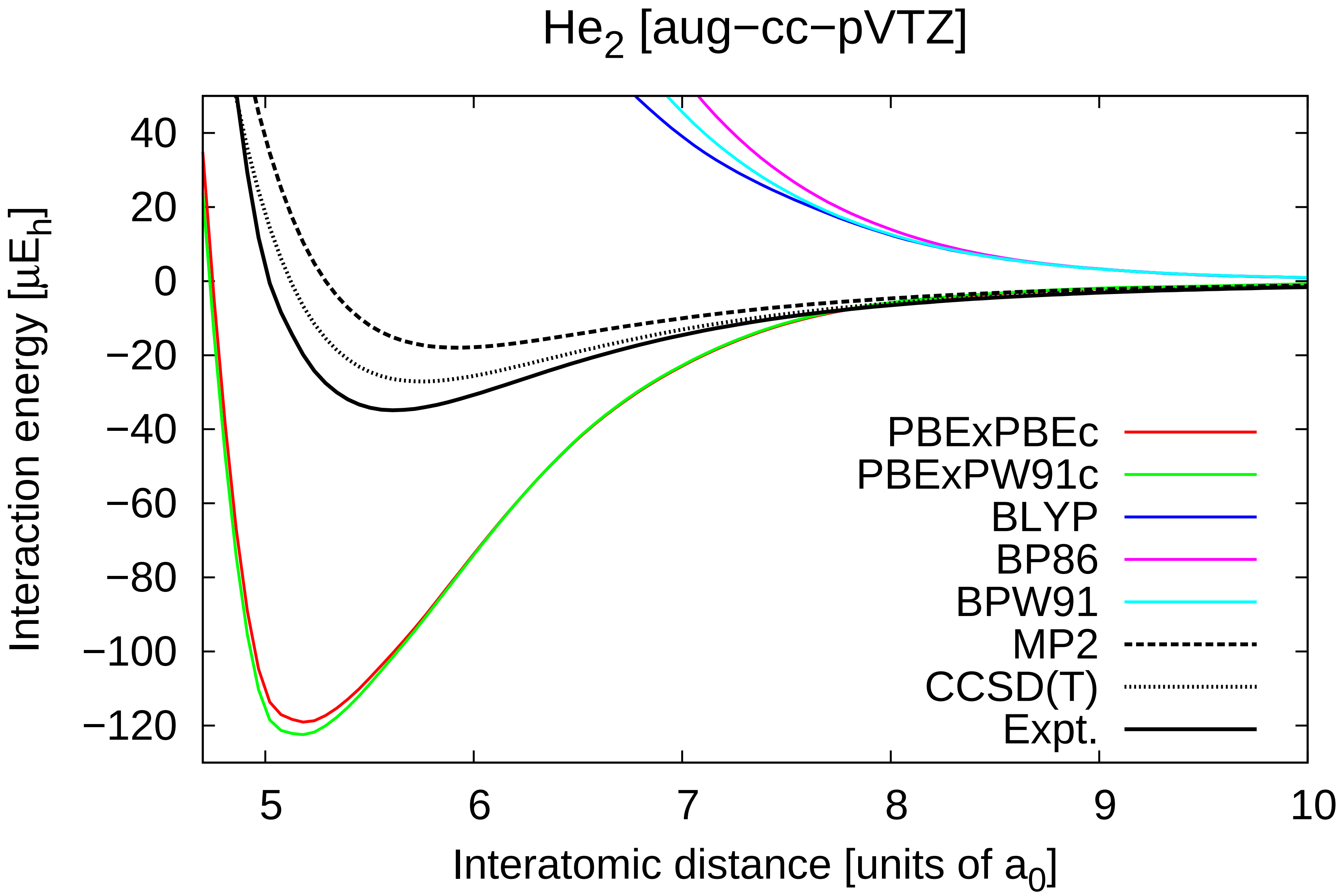
*Yanai, T.; Tew, D. P.; Handy, N. C., Chem. Phys. Lett., 393, 51-57 (**2004**).*

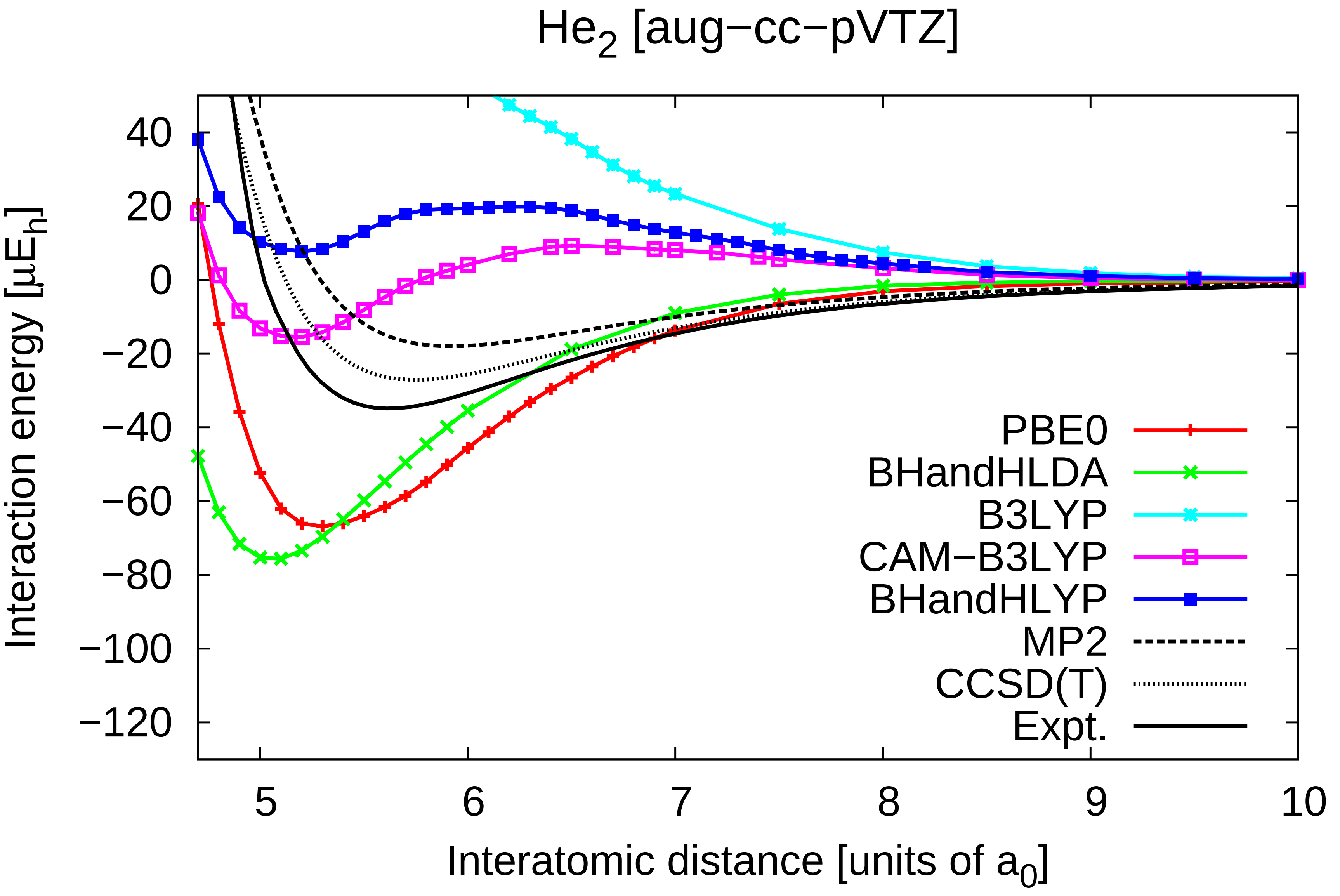
(arbitrary) range separation of the electronic repulsion




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]


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.

Complements

- Decomposition of the xc energy into *exchange* and *correlation* contributions:

$$E_{\rm xc}[n] = E_{\rm x}[n] + E_{\rm c}[n].$$

- *Exact exchange* functional:

$$E_{\rm x}[n] = \left\langle \Phi^{\rm KS}[n] \right| \hat{W}_{\rm ee} \left| \Phi^{\rm KS}[n] \right\rangle - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} {\rm d}\mathbf{r}{\rm d}\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$

- *Exact correlation* functional:

$$\begin{aligned}
E_{\rm c}[n] &= F[n] - T_{\rm s}[n] - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} {\rm d}\mathbf{r}{\rm d}\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - E_{\rm x}[n] \\
&= \langle \Psi[n] | \hat{T} + \hat{W}_{\rm ee} | \Psi[n] \rangle - \left\langle \Phi^{\rm KS}[n] \right| \hat{T} + \hat{W}_{\rm ee} \left| \Phi^{\rm KS}[n] \right\rangle \\
&= \langle \Psi[n] | \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v[n](\mathbf{r}_i) \times | \Psi[n] \rangle - \left\langle \Phi^{\rm KS}[n] \right| \hat{T} + \hat{W}_{\rm ee} + \sum_{i=1}^{N} v[n](\mathbf{r}_i) \times \left| \Phi^{\rm KS}[n] \right\rangle \\
&< 0.
\end{aligned}$$