

Introduction to density-functional theory

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Electronic Hamiltonian

N -electron Hamiltonian (in atomic units) within the Born-Oppenheimer approximation:

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

$$\hat{T} = \sum_{i=1}^N \hat{t}(i) \quad \text{where} \quad \hat{t}(i) \equiv -\frac{1}{2} \nabla_{\mathbf{r}_i}^2 \quad \rightarrow \quad \text{kinetic energy}$$

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

$$\hat{W}_{ee} = \frac{1}{2} \sum_{i \neq j}^N \hat{w}_{ee}(i, j) \quad \text{where} \quad \hat{w}_{ee}(i, j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times \quad \rightarrow \quad \text{electron-electron repulsion}$$

A physical N -electron wavefunction $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ depends on the positions of each electron (spin will be introduced later on) and fulfils the Schrödinger equation $\hat{H}\Psi = E\Psi$.

Rayleigh–Ritz variational principle for the ground state

- Let $\{\Psi_I\}_{I=0,1,2,\dots}$ denote the **exact** orthonormal electronic ground-state ($I = 0$) and excited-state ($I > 0$) wavefunctions:

$$\hat{H}|\Psi_I\rangle = E_I|\Psi_I\rangle, \quad \langle\Psi_I|\Psi_J\rangle = \delta_{IJ}$$

- We assume for clarity that the ground state is **non-degenerate**: $E_I > E_0$ when $I > 0$.
- We will use **real algebra** in the following (non-relativistic quantum chemistry):

$$\langle\Psi|\Phi\rangle = \langle\Phi|\Psi\rangle^* = \langle\Phi|\Psi\rangle$$

- The exact ground-state energy can be expressed as $E_0 = \min_{\Psi} \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_0|\hat{H}|\Psi_0\rangle$

where the minimization is **restricted** to **normalized** wavefunctions Ψ .

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

Rayleigh–Ritz variational principle for the ground state

- Note that, if $\Psi \neq \Psi_0$, then $\langle \Psi | \hat{H} | \Psi \rangle > E_0$.

Proof:

Since $\Psi \neq \Psi_0$, we can find a non-zero integer K such that $C_K \neq 0$, otherwise $C_0^2 = \langle \Psi | \Psi \rangle = 1 \rightarrow \Psi = \Psi_0$ (!).

Consequently,

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle - E_0 &= \sum_{I \neq 0} C_I^2 (E_I - E_0) \\ &= \underbrace{C_K^2}_{> 0} \underbrace{(E_K - E_0)}_{> 0} + \sum_{I \neq 0, K} \underbrace{C_I^2}_{\geq 0} \underbrace{(E_I - E_0)}_{> 0} > 0 \end{aligned}$$

Rayleigh–Ritz variational principle for the excited states

- Note also that the **first excited-state** energy E_1 can be obtained variationally under **normalization** ($\langle\Psi|\Psi\rangle = 1$) and **orthogonality** ($\langle\Psi|\Psi_0\rangle = 0$) **constraints**:

$$E_1 = \min_{\Psi \perp \Psi_0} \langle\Psi|\hat{H}|\Psi\rangle = \langle\Psi_1|\hat{H}|\Psi_1\rangle$$

Proof:

Since $\langle\Psi|\Psi_0\rangle = 0 = C_0$, $|\Psi\rangle = \sum_{I>0} C_I |\Psi_I\rangle$ and

$$\langle\Psi|\hat{H}|\Psi\rangle - E_1 \langle\Psi|\Psi\rangle = \sum_{I>0} C_I^2 (E_I - E_1) \geq 0.$$

- Additional orthogonality constraints ($\langle\Psi|\Psi_1\rangle = 0, \dots$) enable to reach second and higher excited-state energies.

Stationarity condition

- Let us consider a **function** $f : x \mapsto f(x)$ and the Taylor expansion around x_0 through first order in $\delta x = x - x_0$:

$$f(x) = f(x_0 + \delta x) = f(x_0) + \left. \frac{df(x)}{dx} \right|_{x=x_0} \times \delta x + \dots$$

- We denote $\delta f(x_0)$ the expansion of $f(x_0 + \delta x) - f(x_0)$ through first order in δx :

$$\delta f(x_0) = \left. \frac{df(x)}{dx} \right|_{x=x_0} \times \delta x.$$

- x_0 is a **stationary point** for f if $\delta f(x_0) = 0$ for any value of δx .
- In this example, where f is a function, the stationarity condition reads $\left. \frac{df(x)}{dx} \right|_{x=x_0} = 0$.
- **Extrema** of f (minima or maxima) are, for example, stationary points.

- Let us now consider the **energy functional** $E : \Psi \mapsto E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle$ which is, for our purpose, defined on the domain of **normalized wavefunctions** Ψ .

- Note that the electronic wavefunction Ψ is a **function** of the electron coordinates. The energy is a "function" of Ψ ,

$$E[\Psi] = \int d\mathbf{r}_1 \dots \int d\mathbf{r}_N \Psi^*(\mathbf{r}_1, \dots, \mathbf{r}_N) \hat{H} \Psi(\mathbf{r}_1, \dots, \mathbf{r}_N),$$

hence the name **functional**.

- The **normalization condition** $\langle \Psi | \Psi \rangle = 1$ implies $\langle \Psi | \hat{H} - E[\Psi] | \Psi \rangle = 0$.
- If we consider infinitesimal variations $\Psi \rightarrow \Psi + \delta\Psi$ around Ψ that **preserve normalization**, we have $\delta \langle \Psi | \hat{H} - E[\Psi] | \Psi \rangle = 0$, thus leading to $\delta E[\Psi] = 2 \langle \delta\Psi | \hat{H} - E[\Psi] | \Psi \rangle$. Therefore

$$\delta E[\Psi] = 0 \Leftrightarrow \hat{H} | \Psi \rangle = E[\Psi] | \Psi \rangle$$

- **Important conclusion:** both **ground- and excited-state wavefunctions** are **stationary** points for the **energy** functional.

Mathematical interlude: Lagrangian

- Rather than taking into account the **normalization constraint** $1 - \langle \Psi | \Psi \rangle = 0$ explicitly in the derivation of the stationarity condition, it is more convenient to introduce the so-called Lagrangian functional (also referred to as **Lagrangian**),

$$\mathcal{L}[\Psi, \mathcal{E}] = E[\Psi] + \mathcal{E}(1 - \langle \Psi | \Psi \rangle),$$

where \mathcal{E} , which is referred to as **Lagrange multiplier**, is a number that has to be determined.

- The stationarity condition can then be rewritten as

$$\frac{\partial \mathcal{L}[\Psi, \mathcal{E}]}{\partial \mathcal{E}} = 0 \quad \rightarrow \quad 1 - \langle \Psi | \Psi \rangle = 0 \quad \text{normalization condition !}$$

AND

$$\delta \mathcal{L}[\Psi, \mathcal{E}] = 0 \quad \rightarrow \quad 2\langle \delta \Psi | \hat{H} - \mathcal{E} | \Psi \rangle = 0 \quad \text{for any } \delta \Psi \text{ (no constraint)}$$

- Note that, when Ψ is stationary, $\mathcal{E} = E[\Psi]$.

Spin, many-body wavefunction and Pauli principle

- The N -electron wavefunction Ψ (also referred to as many-body wavefunction) should take into account the fact that electrons **move in real space**, hence the variables $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ in Ψ , but it should also describe their **intrinsic angular momentum** (the spin).
- The spin quantum state of an electron is usually denoted σ .
- It can be equal to α or β (i.e. \uparrow or \downarrow).
- Consequently, the additional N variables $\sigma_1, \sigma_2, \dots, \sigma_N$ should be taken into account in Ψ with $\sigma_i = \alpha$ or β for $i = 1, 2, \dots, N$.
- Note that, even though **the spin does not appear explicitly in the (non relativistic) Hamiltonian**, it plays a crucial role in the calculation of the energy spectrum. Indeed, because of the spin, two electrons can occupy the same orbital without violating the Pauli principle.
- For convenience, we will denote $X_i \equiv (\mathbf{r}_i, \sigma_i)$ so that the N -electron wavefunction reads

$$\Psi(X_1, X_2, \dots, X_N).$$

Spin, many-body wavefunction and Pauli principle

- Consequently, the expectation value for the energy reads

$$\langle \Psi | \hat{H} | \Psi \rangle = \int dX_1 \int dX_2 \dots \int dX_N \Psi^*(X_1, X_2, \dots, X_N) \hat{H} \Psi(X_1, X_2, \dots, X_N)$$

where $\int d\mathbf{X}_i = \int_{\mathbb{R}^3} d\mathbf{r}_i \sum_{\sigma_i = \alpha, \beta}$ for $i = 1, 2, \dots, N$.

- A physical N -electron wavefunction should be **antisymmetric** with respect to the permutation $X_i \longleftrightarrow X_j$:

$$\Psi(X_1, \dots, X_i, \dots, X_j, \dots, X_N) = -\Psi(X_1, \dots, X_j, \dots, X_i, \dots, X_N)$$

which can be written in a more compact form as $\Psi(\mathbf{X}) = -\Psi(\mathbf{X}_{i \leftrightarrow j})$. Consequently,

$$\Psi(\mathbf{X}) = \frac{1}{2} \left(\Psi(\mathbf{X}) - \Psi(\mathbf{X}_{i \leftrightarrow j}) \right) \rightarrow \Psi(\mathbf{X}) = 0 \text{ if } X_i = X_j,$$

thus preventing two electrons from being at the same position with the same spin (**Pauli principle**).

Density-functional theory (DFT)

- The exact ground-state energy E_0 can be obtained by **calculating** the associated ground-state **wavefunction** $\Psi_0(X_1, X_2, \dots, X_N)$ explicitly. For that purpose, one should solve the Schrödinger equation or apply the variational principle.
- **FCI** is applicable only to very (very) small molecular systems since it is **computationally expensive**.
- Note that the nuclear-electron attraction contribution to E_0 can be expressed in terms of a much simpler quantity n_0 than the wavefunction, which is called the **ground-state electron density**:

$$E_0 = \langle \Psi_0 | \hat{T} + \hat{W}_{ee} | \Psi_0 \rangle + \underbrace{\int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) n_0(\mathbf{r})}_{(v|n_0)}$$

where

$$n_0(\mathbf{r}) = N \sum_{\sigma_1} \int dX_2 \int dX_3 \dots \int dX_N \left| \Psi_0(\mathbf{r}\sigma_1, X_2, X_3, \dots, X_N) \right|^2$$

- Note that both kinetic and two-electron repulsion contributions to the energy cannot be expressed explicitly in terms of n_0 .

Expectation value of any one-electron potential interaction energy

- 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:

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

where

$$n_{\Psi}(\mathbf{r}) = N \sum_{\sigma_1} \int dX_2 \int dX_3 \dots \int dX_N \left| \Psi(\mathbf{r}\sigma_1, X_2, X_3, \dots, X_N) \right|^2.$$

- In the following we will write the electronic Hamiltonian as $\hat{H} \equiv \hat{T} + \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \times$ where \hat{T} and \hat{W}_{ee} are **universal** contributions (i.e. they do not depend on the nuclei) while the local potential energy $v(\mathbf{r})$ is **molecule-dependent**.
- Note that if Ψ is an N -electron eigenfunction of \hat{H} with energy E , it remains eigenfunction when the local potential is shifted by a constant i.e. $v(\mathbf{r}) \rightarrow v(\mathbf{r}) - \mu$:

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

electron density and density operator

- It is sometimes convenient to introduce the so-called **density operator**

$$\hat{n}(\mathbf{r}) \equiv \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \times \quad \leftarrow \text{Dirac distribution !}$$

for calculating the electron density.

- Since, by definition, $\int_{\mathbb{R}^3} d\mathbf{r}_i f(\mathbf{r}_i) \delta(\mathbf{r} - \mathbf{r}_i) = f(\mathbf{r}) = \int_{\mathbb{R}^3} d\mathbf{r}_i f(\mathbf{r}_i) \delta(\mathbf{r}_i - \mathbf{r})$, we obtain

$$n_{\Psi}(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$$

- Consequently, the local potential operator can be rewritten as

$$\sum_{i=1}^N v(\mathbf{r}_i) \times = \sum_{i=1}^N \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) \delta(\mathbf{r} - \mathbf{r}_i) \times = \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) \hat{n}(\mathbf{r})$$

- Thus, we recover the following useful result $\left\langle \Psi \left| \sum_{i=1}^N v(\mathbf{r}_i) \times \right| \Psi \right\rangle = \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) n_{\Psi}(\mathbf{r})$.

First Hohenberg–Kohn theorem

- Note that $v \rightarrow \Psi_0 \rightarrow E_0$
 $\rightarrow n_0$

- **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

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

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

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

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 variational principle

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

thus leading to

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

* 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

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

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

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

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

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 $n(\mathbf{r}) \rightarrow v[n](\mathbf{r}) \rightarrow \underbrace{\Psi[v[n]]}_{\text{ground-state wavefunction}} = \Psi[n]$

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

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

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

thus leading to $E[n] \geq E_0$

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

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

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

Using auxiliary non-interacting electrons to reach the exact density !

- The energy density functional

$$E[n] = F[n] + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r})n(\mathbf{r})$$

is fully known from the HK functional $F[n]$, for which the **explicit expression is unknown** (!). Still,

$$\textit{unknown} = \textbf{unknown but somehow simpler} + \left(\textit{unknown} - \textbf{unknown but somehow simpler} \right)$$

- **HK1** was formulated for "**fully-interacting**" electrons described by the Hamiltonian

$$\hat{T} + \hat{W}_{\text{ee}} + \sum_{i=1}^N v(\mathbf{r}_i) \times \quad : \quad n(\mathbf{r}) \rightarrow \Psi[n] \rightarrow F[n] = \langle \Psi[n] | \hat{T} + \hat{W}_{\text{ee}} | \Psi[n] \rangle$$

- **HK1** is actually also valid for **non-interacting** (Kohn–Sham) electrons described by the Hamiltonian

$$\hat{T} + \sum_{i=1}^N v(\mathbf{r}_i) \times \quad : \quad n(\mathbf{r}) \rightarrow \Phi^{\text{KS}}[n] \rightarrow T_s[n] = \langle \Phi^{\text{KS}}[n] | \hat{T} | \Phi^{\text{KS}}[n] \rangle$$

Non-interacting electrons

- Once the non-interacting local potential $v(\mathbf{r})$ corresponding to the density of interest n is determined (this is **not trivial**), $T_s[n]$ is easily obtained since $\Phi^{\text{KS}}[n]$ is a **single Slater determinant**.
- Two-electron case: let φ be the normalized solution to the one-electron Schrödinger equation

$$-\frac{1}{2}\nabla_{\mathbf{r}}^2\varphi(\mathbf{r}) + v(\mathbf{r})\varphi(\mathbf{r}) = \varepsilon\varphi(\mathbf{r})$$

with lowest energy ε . Then $\Phi^{\text{KS}}[n] \equiv |\varphi^\alpha \varphi^\beta|$ which gives

$$\Phi^{\text{KS}}[n](\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2) = \frac{1}{\sqrt{2}}\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2)\left(\delta_{\sigma_1\alpha}\delta_{\sigma_2\beta} - \delta_{\sigma_2\alpha}\delta_{\sigma_1\beta}\right).$$

Indeed,

$$\left(\hat{T} + \sum_{i=1}^2 v(\mathbf{r}_i) \times\right)\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) = 2\varepsilon\varphi(\mathbf{r}_1)\varphi(\mathbf{r}_2) \longrightarrow \left(\hat{T} + \sum_{i=1}^2 v(\mathbf{r}_i) \times\right)\Phi^{\text{KS}}[n] = 2\varepsilon\Phi^{\text{KS}}[n]$$

Non-interacting electrons

- The density is simply expressed in terms of the orbital φ as follows

$$\begin{aligned}n(\mathbf{r}) = n_{\Phi^{\text{KS}}[n]}(\mathbf{r}) &= 2 \sum_{\sigma_1, \sigma_2 = \alpha, \beta} \int_{\mathbb{R}^3} d\mathbf{r}_2 \left(\Phi^{\text{KS}}[n](\mathbf{r}, \sigma_1, \mathbf{r}_2, \sigma_2) \right)^2 \\ &= 2 \varphi^2(\mathbf{r})\end{aligned}$$

and the non-interacting kinetic energy equals

$$T_s[n] = \langle \Phi^{\text{KS}}[n] | \hat{T} | \Phi^{\text{KS}}[n] \rangle = 2\varepsilon - \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) n(\mathbf{r}) = 2\varepsilon - 2 \int_{\mathbb{R}^3} d\mathbf{r} v(\mathbf{r}) \varphi^2(\mathbf{r})$$

which finally gives $T_s[n] = 2 \times -\frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{r} \varphi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \varphi(\mathbf{r})$

Non-interacting electrons

- For an **even number** N of electrons the KS determinant with density n can be formally written as

$$\Phi^{\text{KS}}[n] \equiv |\varphi_1^2 \varphi_2^2 \dots \varphi_{\frac{N}{2}}^2|$$

where the KS orbitals φ_i fulfill

$$-\frac{1}{2} \nabla_{\mathbf{r}}^2 \varphi_i(\mathbf{r}) + v_{\text{KS}}[n](\mathbf{r}) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \quad i = 1, \dots, N/2.$$

Note that the local potential $v_{\text{KS}}[n](\mathbf{r})$ is an **implicit functional** of n ensuring that

$$n(\mathbf{r}) = n_{\Phi^{\text{KS}}[n]}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \varphi_i^2(\mathbf{r}).$$

- Once this potential is obtained, the "non-interacting" kinetic energy simply equals

$$T_s[n] = \langle \Phi^{\text{KS}}[n] | \hat{T} | \Phi^{\text{KS}}[n] \rangle = 2 \times \sum_{i=1}^{\frac{N}{2}} -\frac{1}{2} \int_{\mathbb{R}^3} d\mathbf{r} \varphi_i(\mathbf{r}) \nabla_{\mathbf{r}}^2 \varphi_i(\mathbf{r})$$

Kohn–Sham DFT (KS-DFT)

- The non-interacting kinetic energy density functional $T_s[n]$ being unknown but somehow simpler, Kohn and Sham proposed the following decomposition:

$$F[n] = T_s[n] + \underbrace{\left(F[n] - T_s[n] \right)}_?$$

- What are the **physical effects** contained in $F[n] - T_s[n]$?

Let us have a look at the MP2 energy expression for analysis purposes ...

$$E_0 = \langle \Phi^{\text{HF}} | \hat{T} + \hat{V}_{\text{ne}} | \Phi^{\text{HF}} \rangle + \underbrace{\sum_{i,j=1}^{N/2} 2\langle ij|ij \rangle}_{E_{\text{H}}} - \underbrace{\sum_{i,j=1}^{N/2} \langle ij|ji \rangle}_{E_{\text{x}}} + \underbrace{\sum_{a,b,i,j} \frac{\langle ab|ij \rangle (2\langle ab|ij \rangle - \langle ab|ji \rangle)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}}_{E_{\text{c}}} + \dots$$

Kohn–Sham DFT (KS-DFT)

- **Hartree–exchange–correlation** energy functional:

$$E_{\text{Hxc}}[n] = F[n] - T_s[n]$$

- Hartree (or Coulomb) energy in Hartree–Fock (HF): $E_{\text{H}} = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{r}d\mathbf{r}' \frac{n_{\Phi^{\text{HF}}}(\mathbf{r})n_{\Phi^{\text{HF}}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$

→ universal **Hartree functional**

$$E_{\text{H}}[n] = \frac{1}{2} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{r}d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

- Exchange energy in HF:

$$E_{\text{x}} = - \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} d\mathbf{r}d\mathbf{r}' \frac{\sum_{i=1}^{N/2} \varphi_i(\mathbf{r})\varphi_i(\mathbf{r}') \sum_{j=1}^{N/2} \varphi_j(\mathbf{r})\varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = \langle \Phi^{\text{HF}} | \hat{W}_{\text{ee}} | \Phi^{\text{HF}} \rangle - E_{\text{H}}$$

→ universal (implicit) **exchange functional**

$$E_{\text{x}}[n] = \langle \Phi^{\text{KS}}[n] | \hat{W}_{\text{ee}} | \Phi^{\text{KS}}[n] \rangle - E_{\text{H}}[n]$$

Kohn–Sham DFT (KS-DFT)

- Universal **correlation functional**:

$$E_c[n] = E_{\text{Hxc}}[n] - E_{\text{H}}[n] - E_x[n]$$

- According to **HK2** the **exact** ground-state energy equals

$$\begin{aligned} E_0 &= F[n_0] + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r})n_0(\mathbf{r}) \\ &= T_s[n_0] + E_{\text{Hxc}}[n_0] + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r})n_0(\mathbf{r}) \\ &= \langle \Phi^{\text{KS}} | \hat{T} | \Phi^{\text{KS}} \rangle + E_{\text{Hxc}}[n_0] + \int_{\mathbb{R}^3} d\mathbf{r} v_{\text{ne}}(\mathbf{r})n_0(\mathbf{r}) \end{aligned}$$

where $\Phi^{\text{KS}} = \Phi^{\text{KS}}[n_0]$ is the KS determinant with the exact physical (fully-interacting) density n_0 .

- Important conclusion: the **exact** energy is obtained with **one single determinant** in KS-DFT !
- How do we find Φ^{KS} ? All we need to know is actually the Hxc functional $E_{\text{Hxc}}[n]$

Levy–Lieb constrained search formalism

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

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

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

$$\longrightarrow T_s[n] \leq \langle \Psi | \hat{T} | \Psi \rangle \longrightarrow \boxed{T_s[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} | \Psi \rangle}$$

- Therefore $\langle \Phi^{\text{KS}} | \hat{T} | \Phi^{\text{KS}} \rangle = T_s[n_0] = \min_{\Psi \rightarrow n_0} \langle \Psi | \hat{T} | \Psi \rangle$ but we do **not** know n_0 ...
- Note that, as a consequence of the previous equality, $T_s[n_0] \leq \langle \Psi_0 | \hat{T} | \Psi_0 \rangle$!

Kohn–Sham DFT (KS-DFT)

- For **any normalized wavefunction** Ψ ,

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

$$E[n_\Psi] \geq E_0$$

where $\hat{V}_{\text{ne}} \equiv \sum_{i=1}^N v_{\text{ne}}(\mathbf{r}_i) \times$.

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

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

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

Mathematical interlude: functional derivative

- Let $f : x \mapsto f(x)$ 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)

$$f(x_0 + \delta x) = f(x_0) + \left. \frac{df}{dx} \right|_{x=x_0} \times \delta x + \frac{1}{2} \left. \frac{d^2 f}{dx^2} \right|_{x=x_0} \times \delta x^2 + \dots$$

- Let $S : n \mapsto S[n]$ 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 $\frac{\delta S}{\delta n(\mathbf{r})}[n_0]$. The latter is obtained from the Taylor expansion ($\delta n(\mathbf{r})$ is a small variation of the density around n_0):

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

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

Self-consistent KS equations

- The minimization of the KS-DFT-based energy expression must be performed under wavefunction **normalization constraint**, thus leading to the following Lagrangian,

$$\mathcal{L}[\Psi] = \langle \Psi | \hat{T} + \hat{V}_{\text{ne}} | \Psi \rangle + E_{\text{Hxc}}[n_{\Psi}] + \mathcal{E}^{\text{KS}} \left(1 - \langle \Psi | \Psi \rangle \right).$$

- Using the expression $n_{\Psi}(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle$ and the stationarity condition $\delta \mathcal{L}[\Phi^{\text{KS}}] = 0$ leads to

$$\left(\hat{T} + \sum_{i=1}^N \left[v_{\text{ne}}(\mathbf{r}_i) + \frac{\delta E_{\text{Hxc}}[n_{\Phi^{\text{KS}}}]}{\delta n(\mathbf{r}_i)} \right] \times \right) \Phi^{\text{KS}} = \mathcal{E}^{\text{KS}} \Phi^{\text{KS}},$$

or, equivalently, $\Phi^{\text{KS}} \equiv \left| (\varphi_1^{\text{KS}})^2 (\varphi_2^{\text{KS}})^2 \dots (\varphi_{N/2}^{\text{KS}})^2 \right|$, where the KS orbitals $\varphi_i^{\text{KS}}(\mathbf{r})$ fulfill the following **self-consistent equations**,

$$-\frac{1}{2} \nabla_{\mathbf{r}}^2 \varphi_i^{\text{KS}}(\mathbf{r}) + \left(v_{\text{ne}}(\mathbf{r}) + \frac{\delta E_{\text{Hxc}}[n_{\Phi^{\text{KS}}}]}{\delta n(\mathbf{r})} \right) \varphi_i^{\text{KS}}(\mathbf{r}) = \varepsilon_i^{\text{KS}} \varphi_i^{\text{KS}}(\mathbf{r}) \quad i = 1, \dots, N/2,$$

with $n_{\Phi^{\text{KS}}}(\mathbf{r}) = 2 \sum_{i=1}^{N/2} \left| \varphi_i^{\text{KS}}(\mathbf{r}) \right|^2$ and $\mathcal{E}^{\text{KS}} = 2 \sum_{i=1}^{N/2} \varepsilon_i^{\text{KS}}$.

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

Comparing wavefunction theory with KS-DFT

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

↓

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

multideterminantal wave function

↓

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

single determinant

- Standard approximations to $E_{\text{xc}}[n]$:

$$E_{\text{xc}}^{\text{LDA}}[n] = \int_{\mathbb{R}^3} d\mathbf{r} f(n(\mathbf{r})) \quad \longrightarrow \text{local density approximation (LDA)}$$

$$E_{\text{xc}}^{\text{GGA}}[n] = \int_{\mathbb{R}^3} d\mathbf{r} f(n(\mathbf{r}), |\nabla n(\mathbf{r})|) \quad \longrightarrow \text{generalized gradient approximation}$$

$$E_{\text{xc}}^{\text{meta-GGA}}[n] = \int_{\mathbb{R}^3} d\mathbf{r} f\left(n(\mathbf{r}), |\nabla n(\mathbf{r})|, \nabla^2 n(\mathbf{r}), \sum_{i=1}^{N/2} |\nabla \varphi_i(\mathbf{r})|^2\right) \quad \longrightarrow \text{meta-GGA}$$

where f denotes a **function**.

The uniform electron gas as a model system

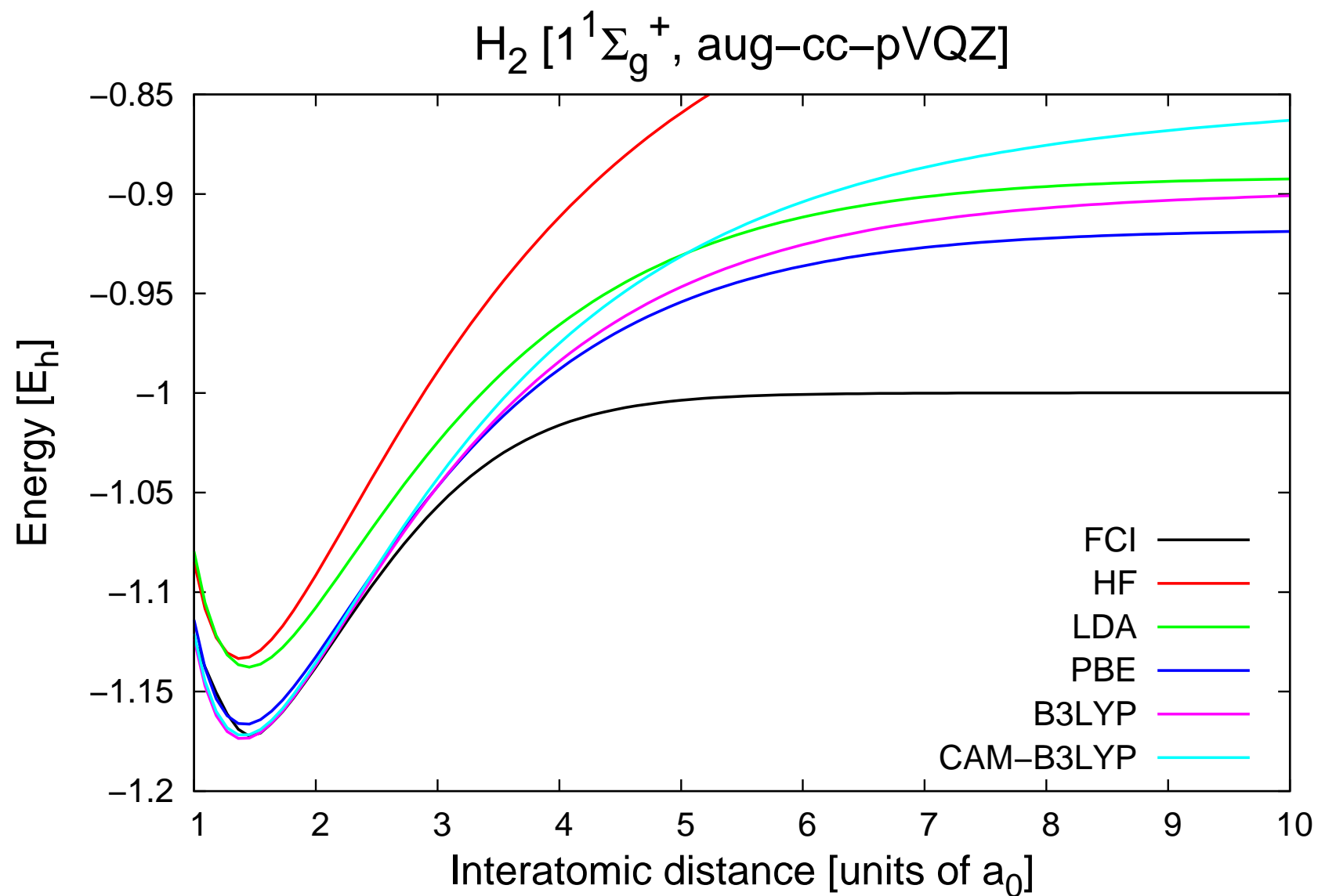
Basic idea:

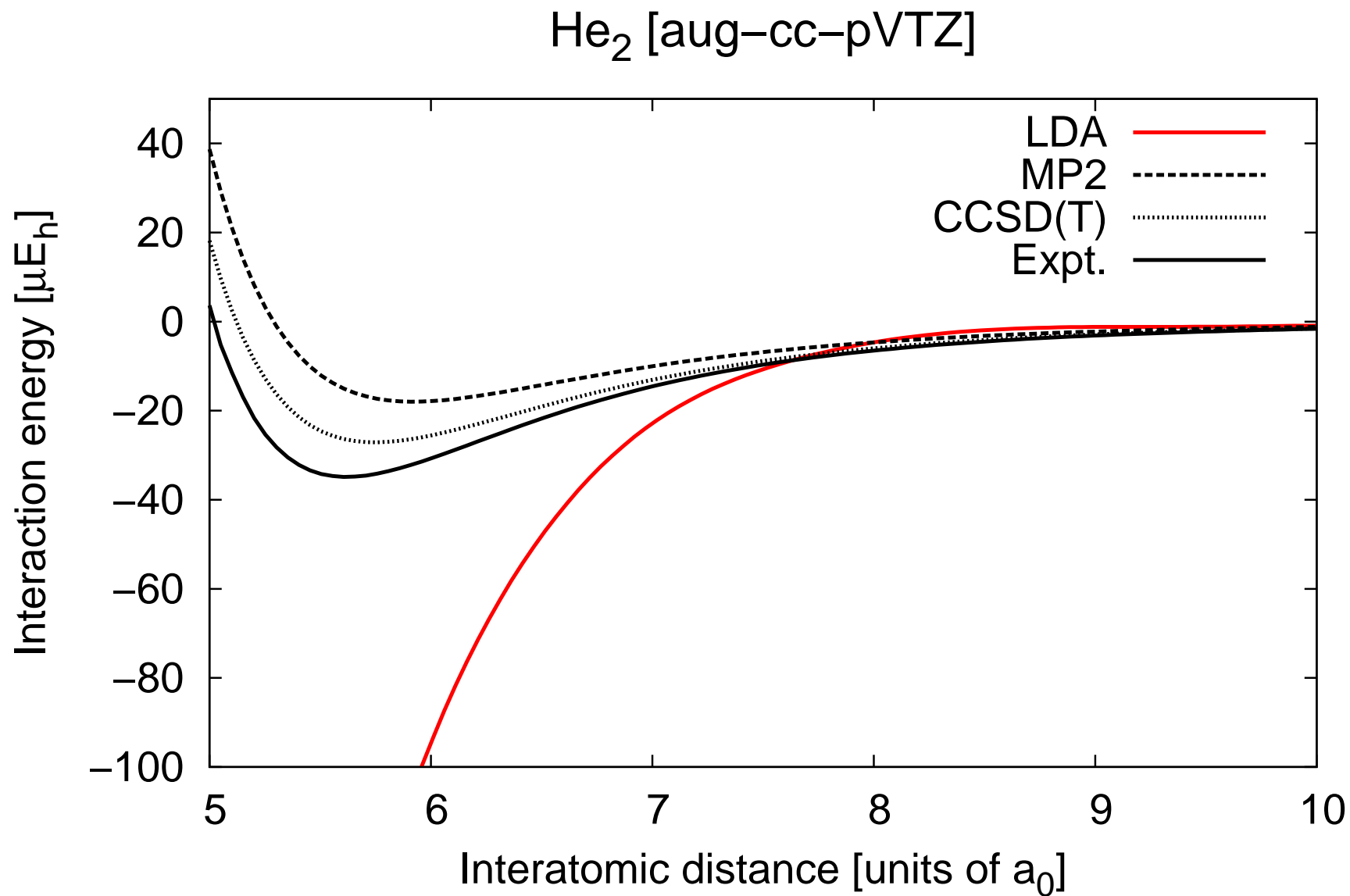
- Let us first consider a single **free particle** in a box with volume $L \times L \times L$ and $L \rightarrow +\infty$. The Schrödinger equation is

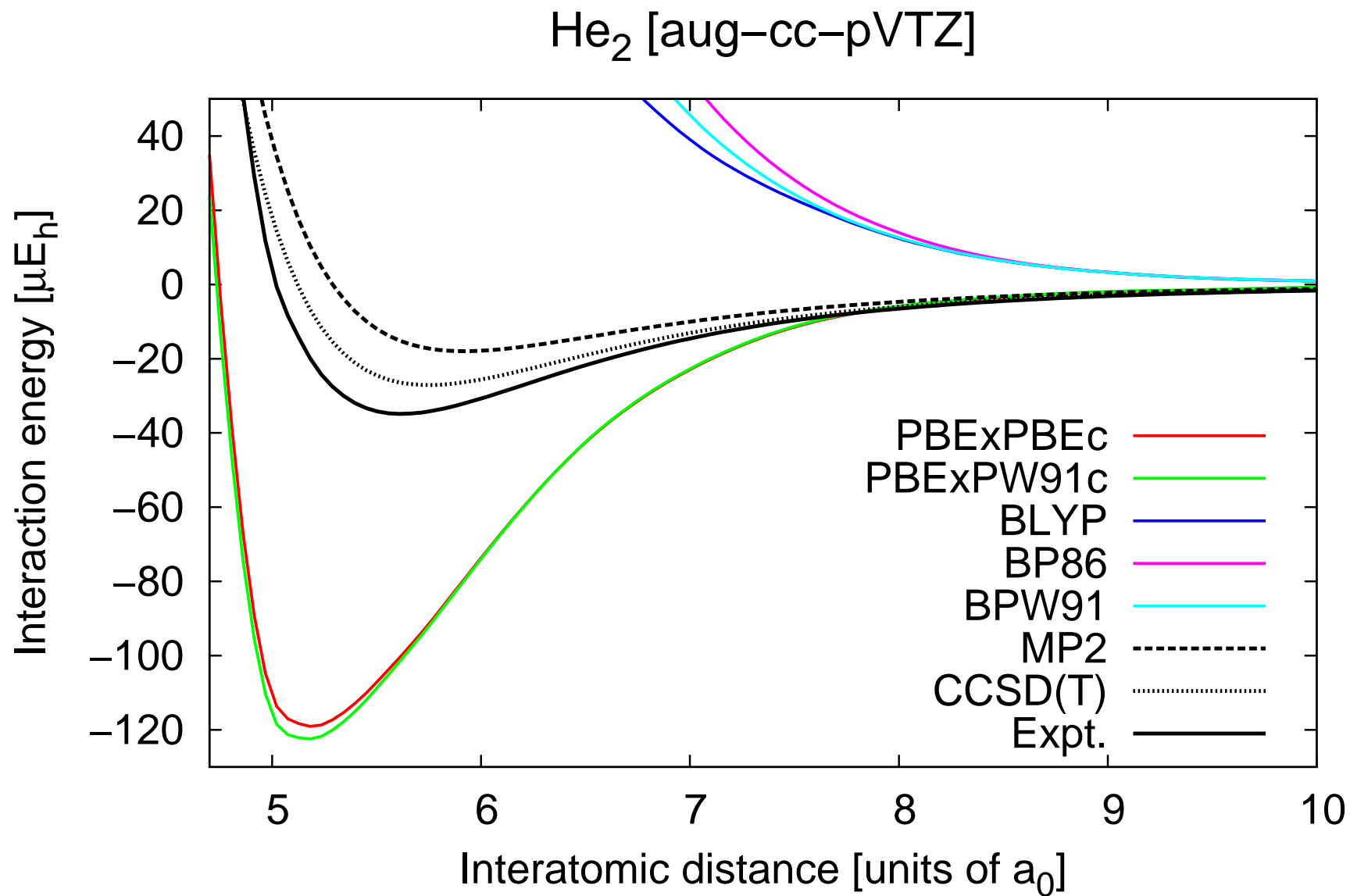
$$-\frac{1}{2} \nabla_{\mathbf{r}}^2 \varphi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} \varphi_{\mathbf{k}}(\mathbf{r})$$

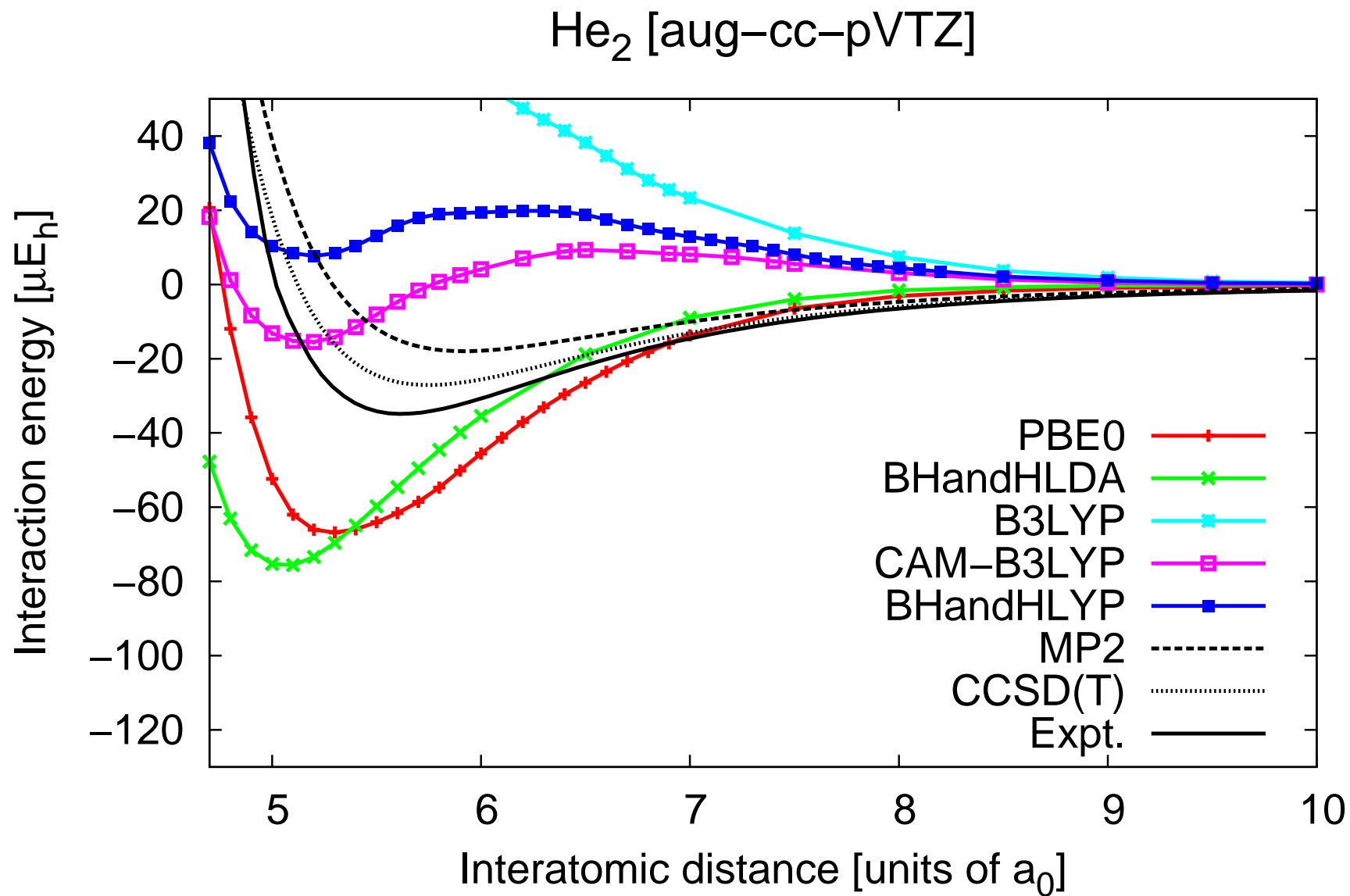
and the solutions are $\varphi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{L^3}} e^{i\mathbf{k} \cdot \mathbf{r}}$ and $\varepsilon_{\mathbf{k}} = k^2/2$ with $\mathbf{k} \equiv (k_x, k_y, k_z)$.

- Note that the wavefunction is **complex**
- In this case the electron density equals $n(\mathbf{r}) = |\varphi_{\mathbf{k}}(\mathbf{r})|^2 = \frac{1}{L^3}$ ← **constant !**
- A large number of electrons N is then introduced into the box. The electron density $n(\mathbf{r}) = N/L^3$ is held constant as $N \rightarrow +\infty$ and $L \rightarrow +\infty$
- The KS system is simply obtained when neglecting the electron-electron repulsions
- **Analytical** expression for the **exchange energy**: $E_x^{\text{LDA}}[n] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3} \int_{\mathbb{R}^3} d\mathbf{r} n^{4/3}(\mathbf{r})$
- **Numerical** calculation of the **correlation energy** (Coupled Cluster, Quantum Monte Carlo)









Linear adiabatic connection

$$\left(\hat{T} + \hat{W}_{ee} + \sum_{i=1}^N v^1(\mathbf{r}_i) \times \right) \Psi = E\Psi \quad \boxed{\lambda = 1}$$



$$\left(\hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v^\lambda(\mathbf{r}_i) \times \right) \Psi^\lambda = \mathcal{E}^\lambda \Psi^\lambda \quad \boxed{0 < \lambda < 1}$$



$$\left(\hat{T} + \sum_{i=1}^N v^0(\mathbf{r}_i) \times \right) \Phi^{\text{KS}} = \mathcal{E}^0 \Phi^{\text{KS}} \quad \boxed{\lambda = 0}$$

$$\boxed{\forall \lambda \in [0, 1] \quad n_\Psi = n_{\Psi^\lambda} = n_{\Phi^{\text{KS}}} = n} \quad \leftarrow \text{density constraint !}$$

- Partially-interacting Levy–Lieb functional: $F^\lambda[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \lambda \hat{W}_{ee} | \Psi \rangle = \langle \Psi^\lambda | \hat{T} + \lambda \hat{W}_{ee} | \Psi^\lambda \rangle$
- **Exact expression** for the correlation energy density functional:

$$E_{\text{Hxc}}[n] = \int_0^1 d\lambda \frac{dF^\lambda[n]}{d\lambda} = \int_0^1 d\lambda \langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \rangle$$

$$\longrightarrow E_c[n] = \int_0^1 d\lambda \underbrace{\left(\langle \Psi^\lambda | \hat{W}_{ee} | \Psi^\lambda \rangle - \langle \Phi^{\text{KS}} | \hat{W}_{ee} | \Phi^{\text{KS}} \rangle \right)}_{\text{correlation integrand } \mathcal{W}_c^\lambda[n]}$$

- **Scaling** relation*:

$$E_c^\lambda[n] = \int_0^\lambda d\nu \left(\langle \Psi^\nu | \hat{W}_{ee} | \Psi^\nu \rangle - \langle \Phi^{\text{KS}} | \hat{W}_{ee} | \Phi^{\text{KS}} \rangle \right) = \lambda^2 E_c[n_{1/\lambda}]$$

where $n_{1/\lambda}$ is the density obtained by **uniform coordinate scaling**: $n_{1/\lambda}(\mathbf{r}) = (1/\lambda)^3 n(\mathbf{r}/\lambda)$

- Correlation integrand written as a density functional: $\mathcal{W}_c^\lambda[n] = \frac{\partial E_c^\lambda[n]}{\partial \lambda}$

*M. Levy and J. P. Perdew, Phys. Rev. B **48**, 11638 (1993).

Legendre–Fenchel transform

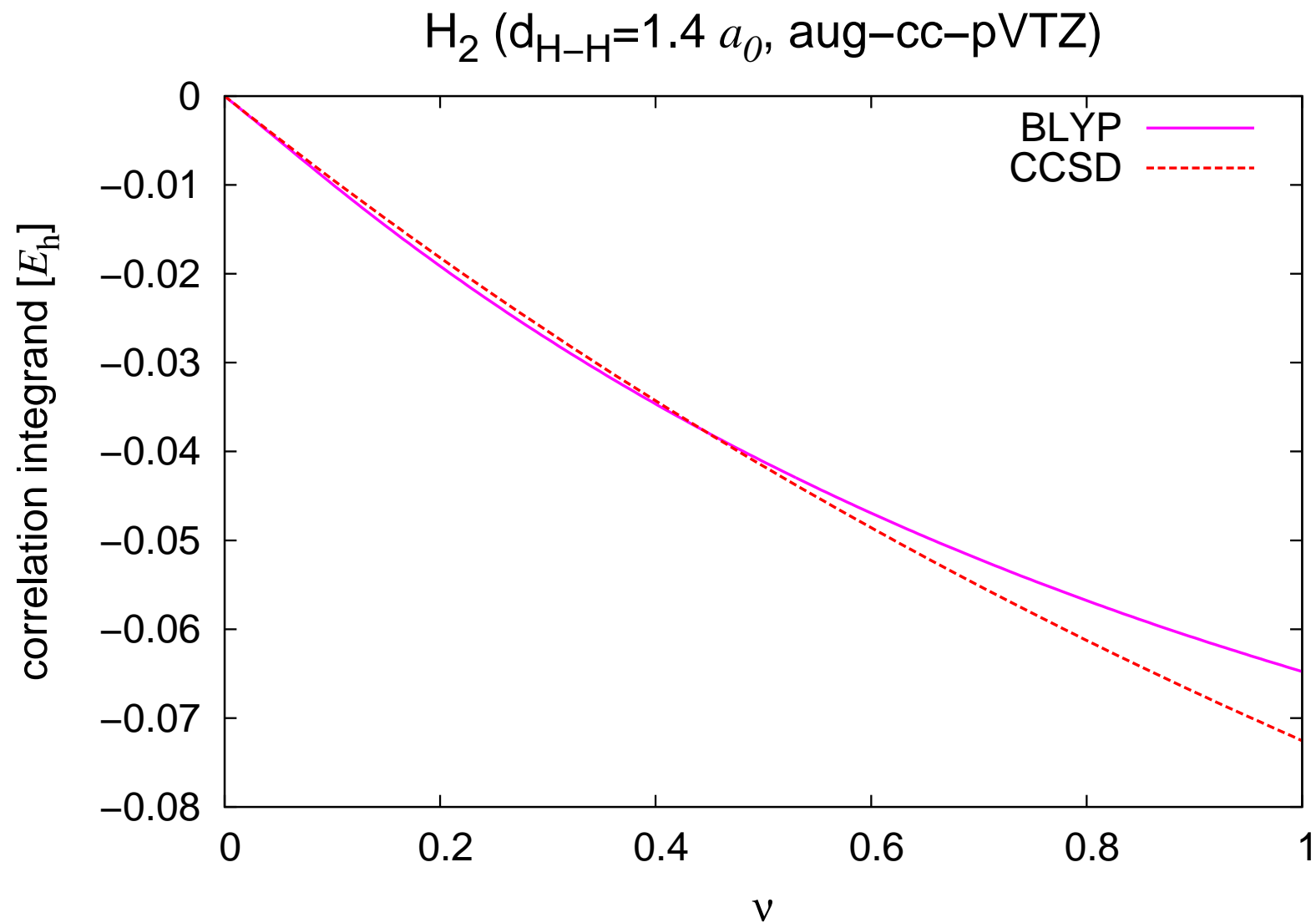
- According to the variational principle, for **any trial potential** $v(\mathbf{r})$, the following inequality is fulfilled,

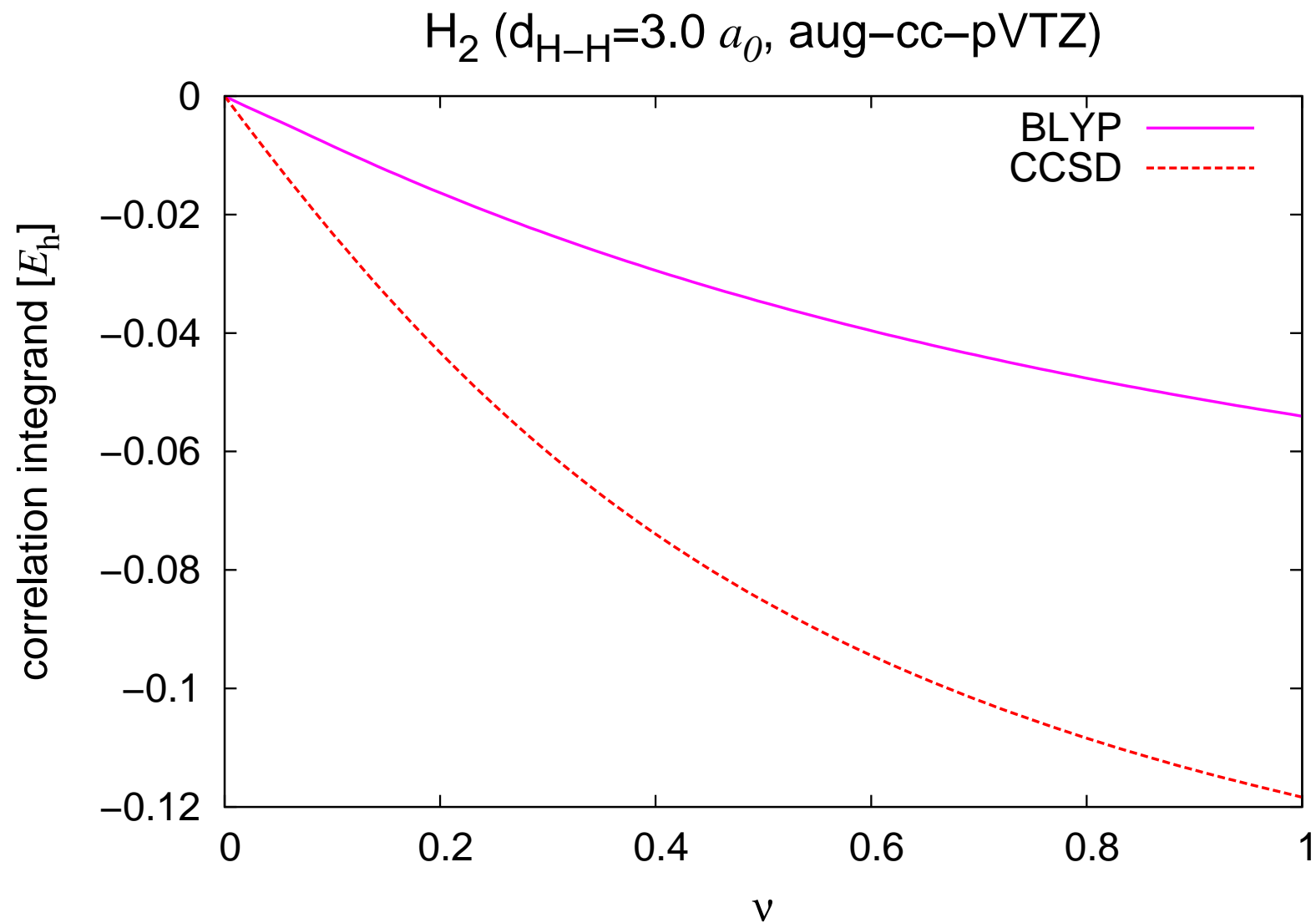
$$\left\langle \Psi^\lambda \left| \hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \times \right| \Psi^\lambda \right\rangle \geq \mathcal{E}^\lambda[v]$$

where $\mathcal{E}^\lambda[v]$ is the ground-state energy of $\hat{T} + \lambda \hat{W}_{ee} + \sum_{i=1}^N v(\mathbf{r}_i) \times$, thus leading to

$$F^\lambda[n] = \sup_v \left\{ \mathcal{E}^\lambda[v] - \int d\mathbf{r} v(\mathbf{r})n(\mathbf{r}) \right\}$$

- Note that the **maximizing potential** is v^λ .
- In the particular case $\lambda = 0$, the Legendre–Fenchel transform enables to calculate the **exact KS potential**.
- By varying λ in the range $0 \leq \lambda \leq 1$ we can fully construct the adiabatic connection.





For the *ab initio* calculation (CCSD) of the adiabatic connection see

A.M. Teale, S. Coriani and T. Helgaker, J. Chem. Phys. 130, 104111 (2009).

A.M. Teale, S. Coriani and T. Helgaker, J. Chem. Phys. 132, 164115 (2010).

A.M. Teale, S. Coriani and T. Helgaker, J. Chem. Phys. 133, 164112 (2010).