Quantum embedding in electronic structure theory

Part 1: The electronic structure problem in Chemistry

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Before we start…

Before we start…

Happy new year!

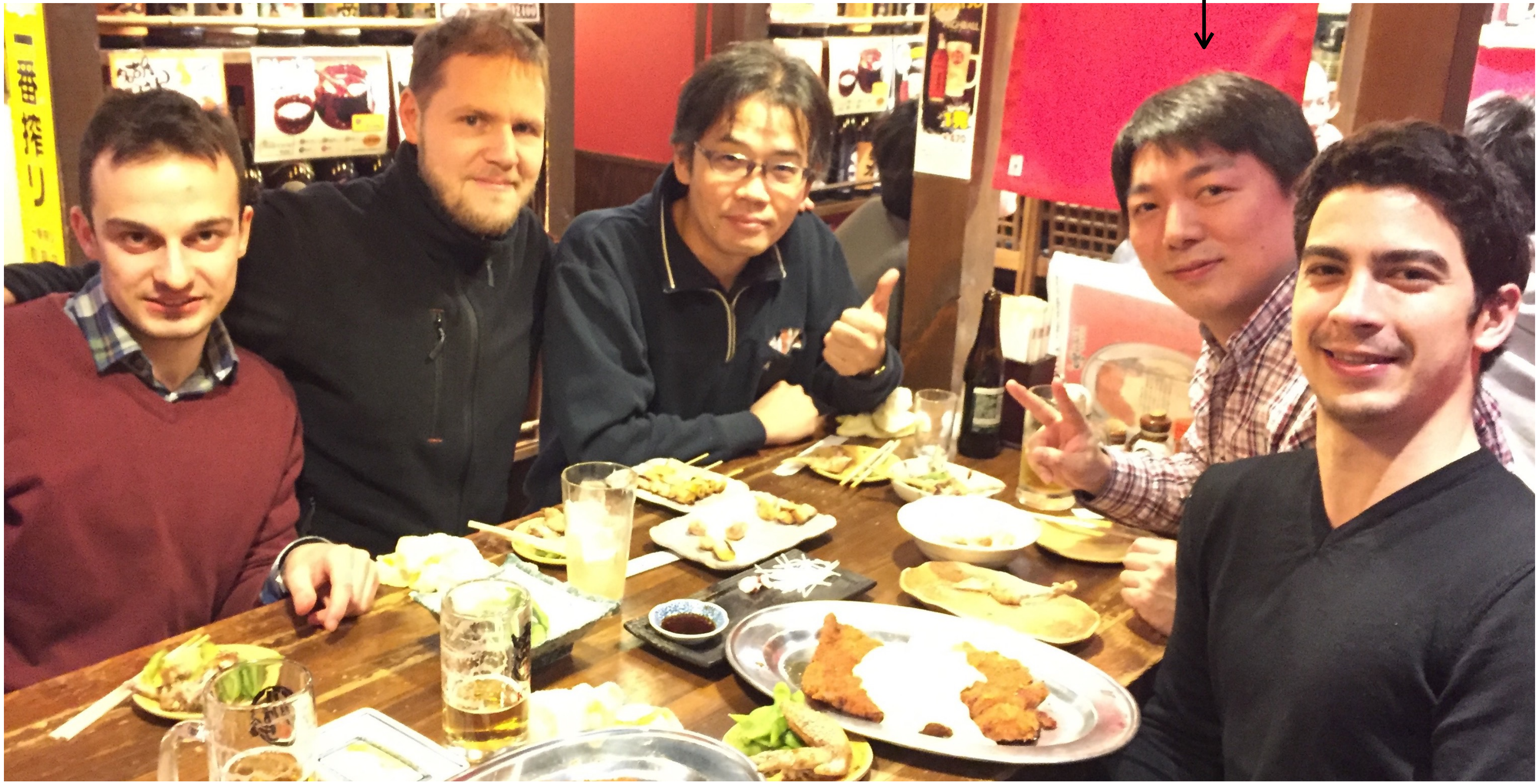
Before we start…

Thanks a lot to Professor Naoki Nakatani for the kind invitation.

Before we start…

Nagoya, February 2017.

Professor Naoki Nakatani



From left to right: **L. Mazouin**, **E.F.**, **M. Tsuchiizu** *(now in Nara)*, **N.N.**, **B. Senjean** *(now in Montpellier, France)*

Before we start…

In order to follow the ***first part*** of the course you only need basic knowledge in ***first quantization.***

Before we start…

I will use ***second quantization*** in the *second and third parts* of the course.

Before we start…

I will use ***second quantization*** in the *second and third parts* of the course.

An *introductory two-hour lecture* on second quantization is available on YouTube:

https://www.youtube.com/watch?v=FQBrEI57pDA

The corresponding slides are available online:

https://quantique.u-strasbg.fr/lib/exe/fetch.php?media=en:pageperso:ef:istpc2021_second_quantization.pdf

Outline

The two main approaches to the ***electronic structure problem*** in Quantum Chemistry will be reviewed.

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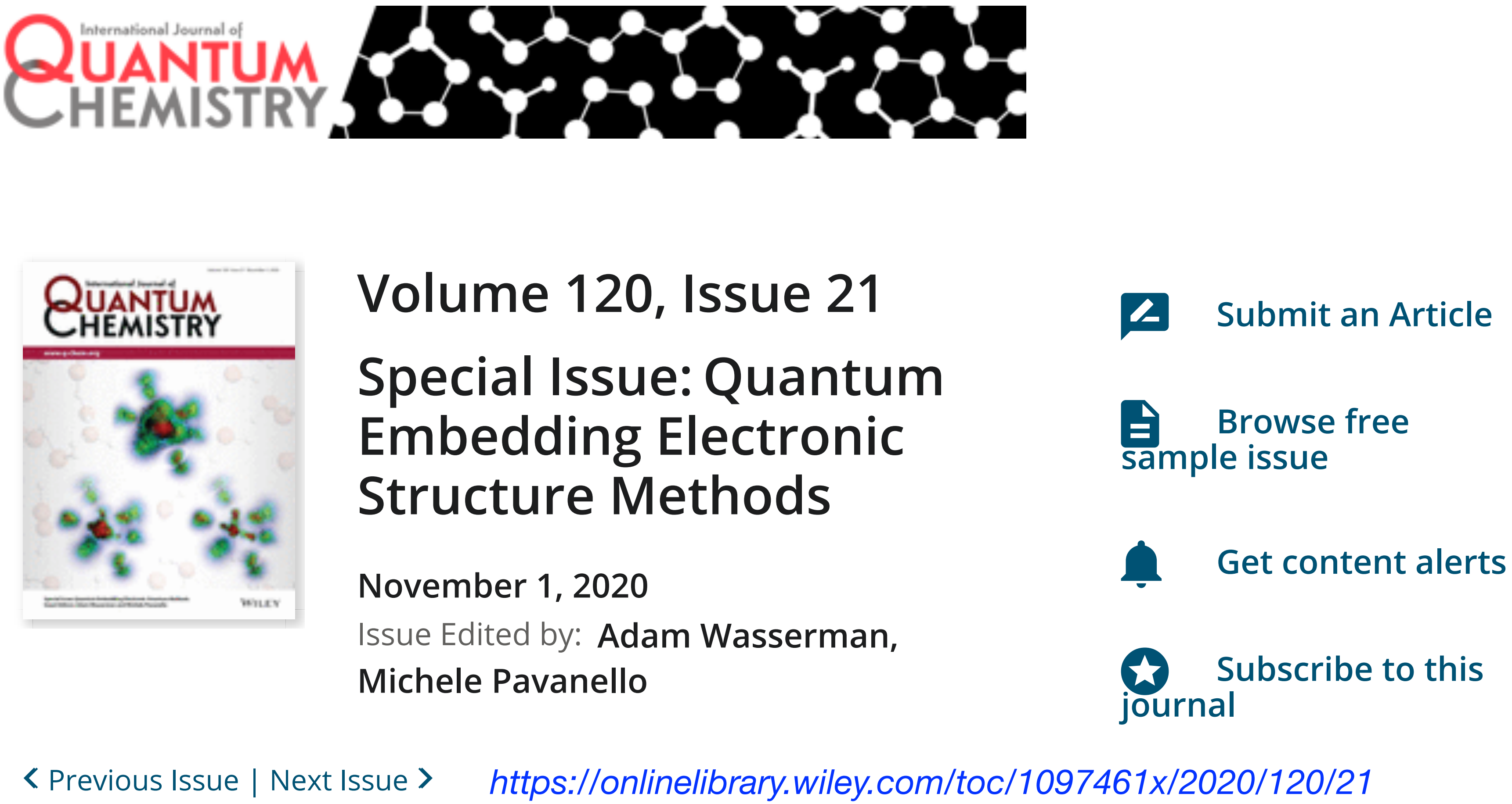
The two main approaches to the ***electronic structure problem*** in Quantum Chemistry will be reviewed.

These approaches are ***wave function theory*** (WFT) and ***density-functional theory*** (DFT).

Limitations of DFT in the description of ***strong electron correlation*** will be highlighted.

This first part of the course aims at ***motivating*** the development of ***quantum embedding*** approaches based on DFT and/or WFT .

Diversity of quantum embedding approaches in Physics and Chemistry



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Electronic Schrödinger equation

$$\hat{H}\Psi_I = E_I\Psi_I$$

Electronic Schrödinger equation

$$\boxed{\hat{H}}\Psi_I = E_I\Psi_I$$

Electronic Hamiltonian
operator

Electronic Schrödinger equation

$$\boxed{\hat{H}}\Psi_I = E_I\Psi_I$$

Electronic Hamiltonian
operator

known!

Electronic Schrödinger equation

$$\hat{H}\Psi_I = \boxed{E_I}\Psi_I$$

Ground $(I = 0)$ *and excited* $(I > 0)$
electronic energies

Electronic Schrödinger equation

$$\hat{H}\Psi_I = \boxed{E_I}\Psi_I$$

Ground $(I = 0)$ *and excited* $(I > 0)$
electronic energies

unknown!

Electronic Schrödinger equation

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

In this lecture we will focus on the ***ground-state problem***

Electronic Schrödinger equation

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

Ground-state electronic
wave function

Electronic Schrödinger equation

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

Ground-state electronic
wave function

unknown!

N-electron wave function

$$\Psi_0 \equiv \Psi_0(\underbrace{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N}_{\textit{electronic } \textbf{\textit{coordinates}}})$$

N-electron wave function

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

*electronic **coordinates***

$$\mathbf{x}_i \equiv \left(\mathbf{r}_i, \sigma_i\right)$$

*Cartesian **space** coordinates*

***Spin** coordinate*

$$\mathbf{r}_i \equiv \left(x_i, y_i, z_i\right)$$

$$\sigma_i = \uparrow \textbf{ or } \downarrow$$

N-electron Hamiltonian operator *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2}\sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part

Two-electron part

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Kinetic energy+nuclear attraction

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

Universal one-electron
differential operator

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Kinetic energy*+nuclear attraction*

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

$$\nabla^2_{\mathbf{r}_i} \equiv \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Electronic repulsion

N**-electron Hamiltonian** *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2}\sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

One-electron
local *(multiplicative)*
operator

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i)\,\times$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times$$

*Kinetic energy+**nuclear attraction***

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

not universal!

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

$$v_{\text{ext}}(\mathbf{r}_i) = -\sum_{A}^{nuclei} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$$

“external” potential energy

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Atomic number

$$v_{\text{ext}}(\mathbf{r}_i) = -\sum_{A}^{nuclei} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$$

Electron-nucleus distance

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part

Two-electron part

We solve the electronic problem
for ***fixed nuclei positions*** $\mathbf{R}_A \equiv (x_A, y_A, z_A)$

$$v_{\text{ext}}(\mathbf{r}_i) = - \sum_{A}^{nuclei} \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|}$$

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part **Two-electron part**

We solve the electronic problem
for ***fixed nuclei positions*** $\mathbf{R}_A \equiv (x_A, y_A, z_A)$

Born-Oppenheimer approximation

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Electronic repulsion

N-**electron Hamiltonian** *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part

Two-electron part

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

Kinetic energy+nuclear attraction

Two-electron
local *(multiplicative)*
operator

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

$$\hat{H} \equiv \sum_{i=1}^{N} \hat{h}(i) + \frac{1}{2} \sum_{i \neq j}^{N} \hat{g}(i,j)$$

One-electron part

Two-electron part

$$\hat{h}(i) \equiv -\frac{1}{2}\nabla^2_{\mathbf{r}_i} + v_{\text{ext}}(\mathbf{r}_i) \times$$

universal!

$$\hat{g}(i,j) \equiv \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \times$$

Kinetic energy+nuclear attraction

Electronic repulsion

N-electron ground-state Schrödinger equation

In summary, we have to solve the following ***differential equation***…

$$-\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i}\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_N,\sigma_N)$$

$$+\sum_{i=1}^{N}v_{\mathrm{ext}}(\mathbf{r}_i)\times\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_N,\sigma_N)$$

$$+\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\times\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_j,\sigma_j\ldots,\mathbf{r}_N,\sigma_N)$$

$$=E_0\times\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N)$$

N-electron ground-state Schrödinger equation

In summary, we have to solve the following ***differential equation***…

$$-\frac{1}{2}\sum_{i=1}^{N}\nabla^2_{\mathbf{r}_i}\overset{?}{\Psi}_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_N,\sigma_N)$$

$$+\sum_{i=1}^{N}v_{\mathrm{ext}}(\mathbf{r}_i)\times\overset{?}{\Psi}_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_N,\sigma_N)$$

$$+\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\times\overset{?}{\Psi}_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_j,\sigma_j\ldots,\mathbf{r}_N,\sigma_N)$$

$$=\overset{?}{E}_0\times\overset{?}{\Psi}_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N)$$

N-electron ground-state Schrödinger equation

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$$+\sum_{i=1}^{N}v_{\rm ext}(\mathbf{r}_i)\times\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_N,\sigma_N)$$

$$+\frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}\times\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_i,\sigma_i,\ldots,\mathbf{r}_j,\sigma_j\ldots,\mathbf{r}_N,\sigma_N)$$

… and we have to find the ***lowest energy (!)***

$$=\overset{?}{E_0}\times\Psi_0(\mathbf{r}_1,\sigma_1,\ldots,\mathbf{r}_N,\sigma_N)$$

Rayleigh-Ritz variational principle

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

Rayleigh-Ritz variational principle

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

Minimisation *over*

trial *normalised* ***wave functions*** Ψ

Rayleigh-Ritz variational principle

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

↓

Minimisation over
trial ***normalised*** *wave functions* Ψ

↓

$$\boxed{\langle \Psi | \Psi \rangle = \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \right|^2 = 1}$$

Rayleigh-Ritz variational principle

$$\int d\mathbf{x}_i \equiv \int d\mathbf{r}_i \sum_{\sigma_i=\uparrow,\downarrow} \equiv \sum_{\sigma_i=\uparrow,\downarrow} \int_{-\infty}^{+\infty} dx_i \int_{-\infty}^{+\infty} dy_i \int_{-\infty}^{+\infty} dz_i$$

$$\langle \Psi | \Psi \rangle = \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \right|^2 = 1$$

Rayleigh-Ritz variational principle

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

Energy expectation value

for the trial wave function Ψ

Rayleigh-Ritz variational principle

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

Energy expectation value

for the trial wave function Ψ

Expectation value *for an observable* $\mathcal{O}$ *described by the* ***quantum operator*** $\hat{\mathcal{O}}$

$$\langle \Psi | \hat{\mathcal{O}} | \Psi \rangle = \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \, \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \times \hat{\mathcal{O}} \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N)$$

$$\overset{notation}{=} \langle \hat{\mathcal{O}} \rangle_{\Psi}$$

Hartree-Fock theory

$$E_0 \approx \min_{\Phi} \langle \Phi | \hat{H} | \Phi \rangle = \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle = E_{HF}$$

Minimization over single Slater determinants

(fully occupied or unoccupied spin-orbitals)

Hartree-Fock theory

$$E_0 \approx \min_{\Phi} \langle \Phi | \hat{H} | \Phi \rangle = \langle \Phi_{HF} | \hat{H} | \Phi_{HF} \rangle = E_{HF}$$

Minimization over single Slater determinants
(fully occupied or unoccupied spin-orbitals)

Hartree-Fock energy
(full exact exchange
and no correlation)

Density-functional theory (DFT)

The Nobel Prize in Chemistry 1998

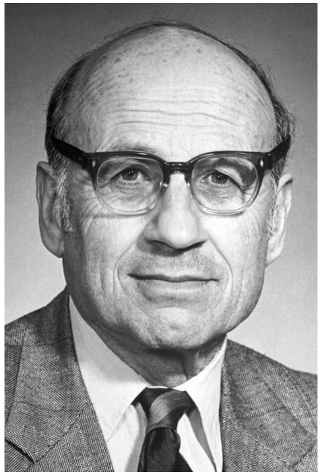


Photo from the Nobel Foundation archive.

Walter Kohn

Prize share: 1/2

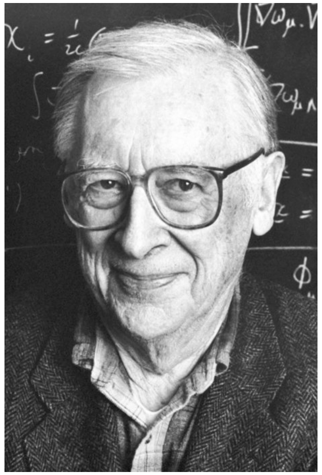


Photo from the Nobel Foundation archive.

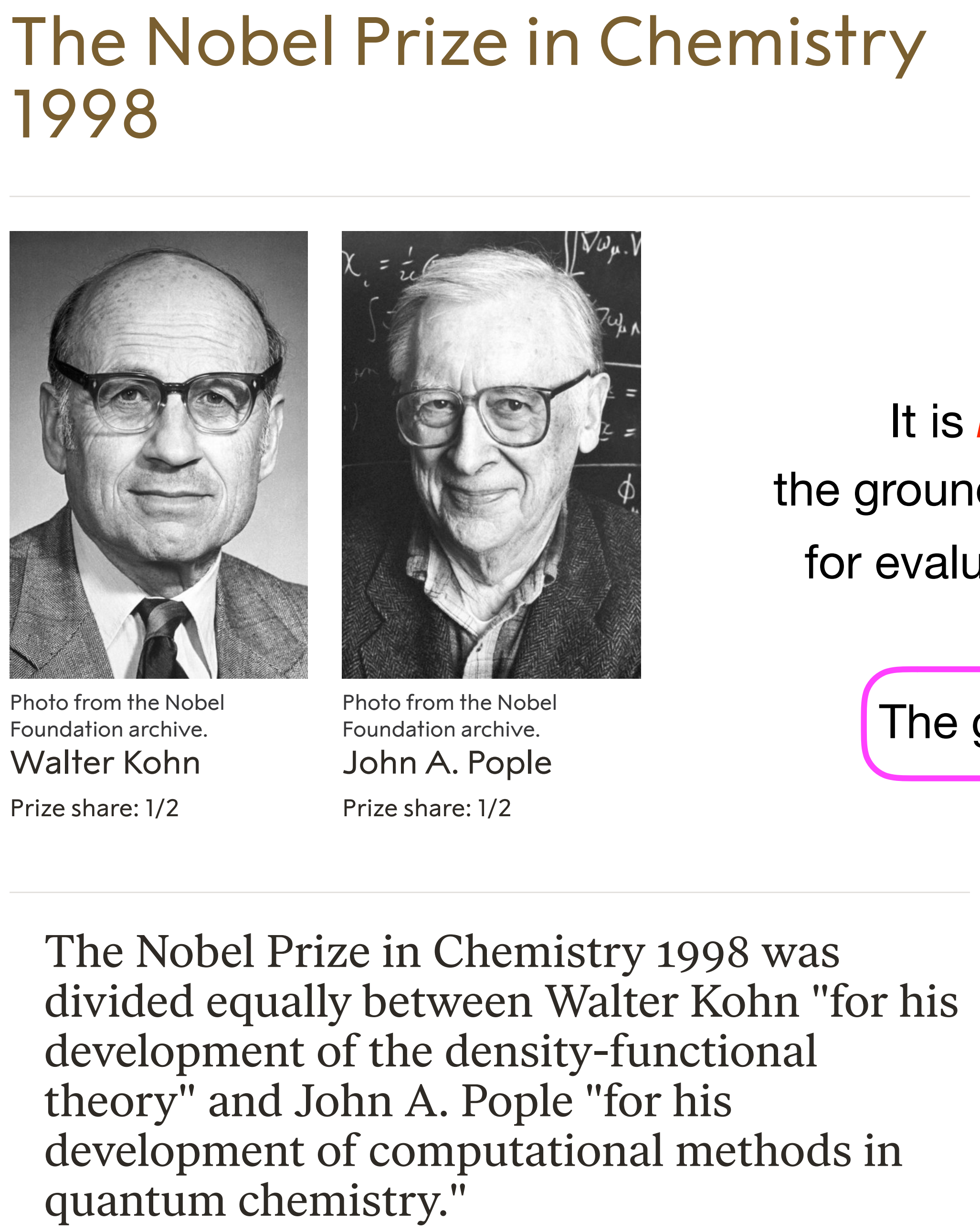
John A. Pople

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.***

Electron density

$$n_{\Psi}(\mathbf{r}) \overset{\textit{definition}}{=} N \sum_{\sigma_1=\uparrow,\downarrow} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \left|\Psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N)\right|^2$$

***Density** of the many-electron wave function* Ψ

Electron density

$$n_{\Psi}(\mathbf{r}) \overset{definition}{=} N \sum_{\sigma_1=\uparrow,\downarrow} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \left| \Psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \right|^2$$

***Density** of the many-electron wave function* Ψ

*Function of the **three** cartesian **space coordinates*** $\mathbf{r} \equiv (x, y, z)$

Electron density

$$n_{\Psi}(\mathbf{r}) \overset{\textit{definition}}{=} N \sum_{\sigma_1=\uparrow,\downarrow} \int d\mathbf{x}_2 \dots \int d\mathbf{x}_i \dots \int d\mathbf{x}_N \left| \Psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \dots, \mathbf{x}_i, \dots, \mathbf{x}_N) \right|^2$$

$$\int d\mathbf{r}\, n_{\Psi}(\mathbf{r}) = N\langle\Psi\,|\,\Psi\rangle = N$$ ⟵ ***Number of electrons***

Electron density

$$n_{\Psi}(\mathbf{r}) \overset{\textit{definition}}{=} N \sum_{\sigma_1=\uparrow,\downarrow} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \, \left| \Psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \right|^2$$

$$n_{\Psi_0}(\mathbf{r}) = n_0(\mathbf{r})$$

← ***Exact ground-state density***

Electron density

$$n_{\Psi}(\mathbf{r}) \overset{definition}{=} N \sum_{\sigma_1=\uparrow,\downarrow} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \left| \Psi(\mathbf{r}, \sigma_1, \mathbf{x}_2, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \right|^2$$

Note that the ***external potential energy*** *is an* ***explicit*** *functional of the* ***density***

Proof:

$$\left\langle \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i) \times \right\rangle_{\Psi} = \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_N \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i) \times \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \right|^2$$

Electrons are indistinguishable particles

$$= \sum_{i=1}^{N} \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \, v_{\text{ext}}(\mathbf{r}_i) \times \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N) \right|^2$$

$\mathbf{x}_1 \leftrightarrow \mathbf{x}_i$

$$= \sum_{i=1}^{N} \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_i \ldots \int d\mathbf{x}_N \, v_{\text{ext}}(\mathbf{r}_i) \times \left| \Psi(\mathbf{x}_i, \ldots, \mathbf{x}_1, \ldots, \mathbf{x}_N) \right|^2$$

$$= \sum_{i=1}^{N} \left(\int d\mathbf{x}_1 \ldots \int d\mathbf{x}_N \, v_{\text{ext}}(\mathbf{r}_1) \times \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \right|^2 \right)$$

Change of variables in the integrals

$\mathbf{x}_i \rightarrow \mathbf{x}_1$

$\mathbf{x}_1 \rightarrow \mathbf{x}_i$

$$= N \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_N \, v_{\text{ext}}(\mathbf{r}_1) \times \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \right|^2$$

$$= \int d\mathbf{r}_1 \, v_{\text{ext}}(\mathbf{r}_1) \times N \sum_{\sigma_1 = \uparrow,\downarrow} \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \left| \Psi(\mathbf{r}_1, \sigma_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \right|^2$$

$$= \int d\mathbf{r}_1 \, v_{\text{ext}}(\mathbf{r}_1) \times n_{\Psi}(\mathbf{r}_1)$$

Exact external potential energy

$$\left\langle \sum_{i=1}^{N} v_{\mathrm{ext}}(\mathbf{r}_i) \times \right\rangle_{\Psi_0} = \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r}) n_{\Psi_0}(\mathbf{r}) = \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r}) \boxed{n_0(\mathbf{r})}$$

$\downarrow$

We do not need to know Ψ_0

Exact external potential energy

$$\left\langle \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i) \times \right\rangle_{\Psi_0} = \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n_{\Psi_0}(\mathbf{r}) = \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) \boxed{n_0(\mathbf{r})}$$

We do not need to know Ψ_0

We just need to know n_0

Exact external potential energy

$$\left\langle \sum_{i=1}^{N} v_{\mathrm{ext}}(\mathbf{r}_i) \times \right\rangle_{\Psi_0} = \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r}) n_{\Psi_0}(\mathbf{r}) = \int d\mathbf{r}\, v_{\mathrm{ext}}(\mathbf{r}) \boxed{n_0(\mathbf{r})}$$

We do not need to know Ψ_0

We just need to know n_0

*The exact **kinetic** and two-electron **repulsion** energies are **implicit** functionals of* n_0.

Levy's constrained search formalism

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

Levy's constrained search formalism

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

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

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

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

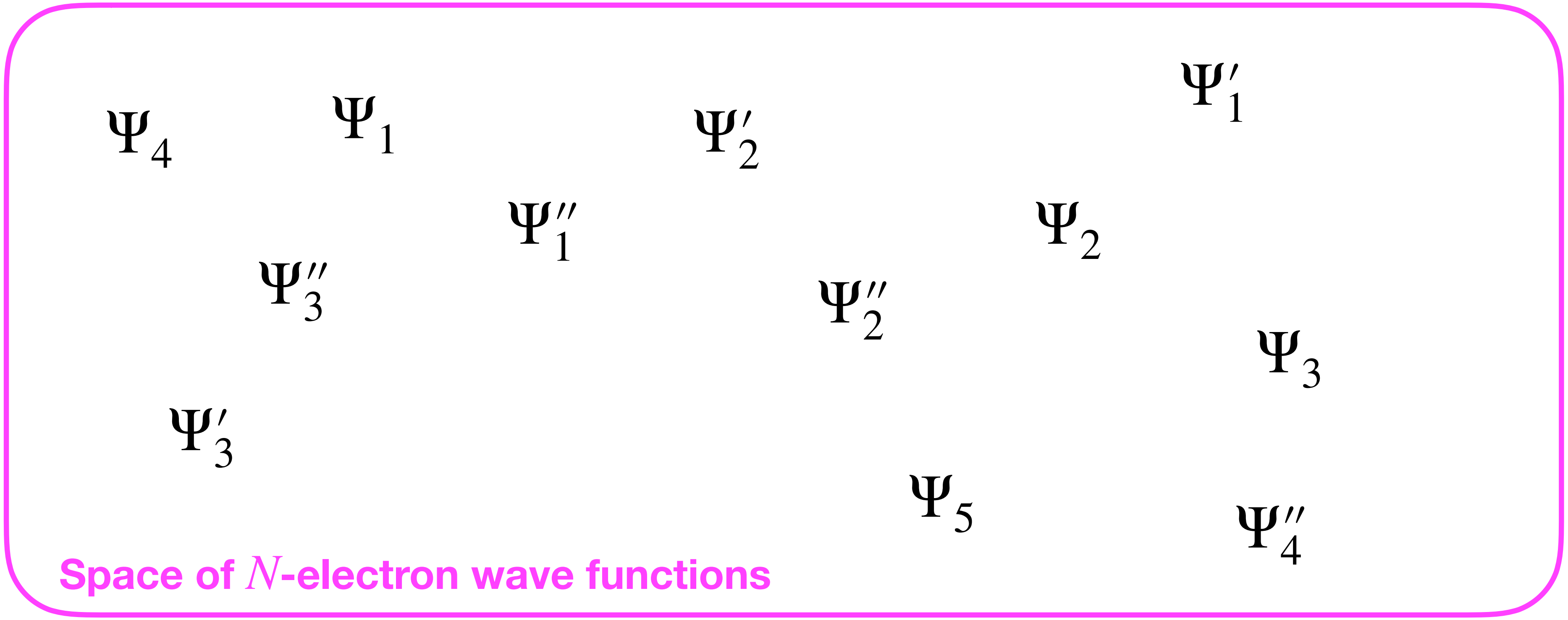
Minimisation over ***densities*** n

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

Levy's constrained search formalism

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

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



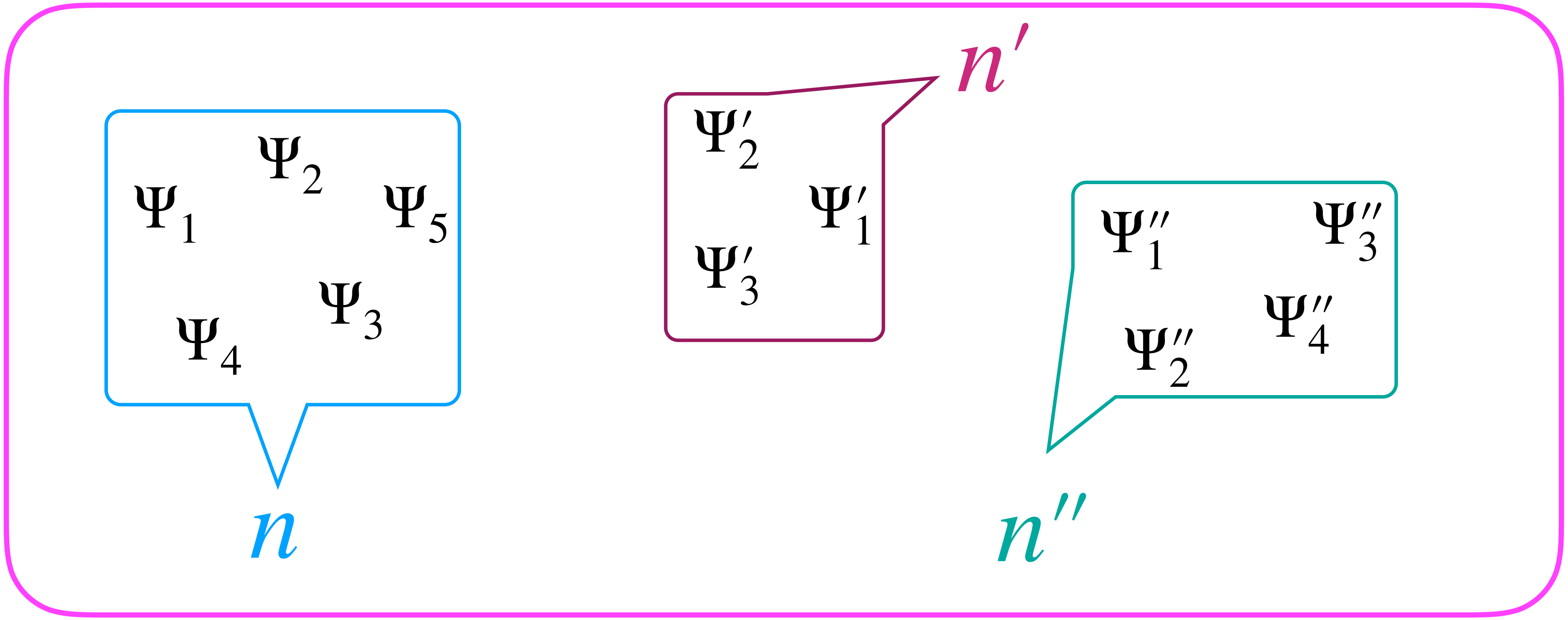
Space of N-electron wave functions

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

Levy's constrained search formalism

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

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



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

Levy's constrained search formalism

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

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

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

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

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

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

Levy's constrained search formalism

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

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

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

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

Levy's constrained search formalism

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

Levy’s constrained search formalism

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

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

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

Kohn-Sham DFT formalism

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

Interacting universal functional

Non-interacting
(kinetic energy) functional

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

Kohn-Sham DFT formalism

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

Interacting universal functional

Non-interacting
(kinetic energy) functional

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

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

Kohn-Sham DFT formalism

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

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*

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

← ***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*

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

←

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

$$
\begin{aligned}
E_0 &= \min_{n}\left\{ F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \right\} \\
&= \min_{n}\left\{ T_{\text{s}}[n] + E_{\text{Hxc}}[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \right\} \\
&= \min_{n}\left\{ \min_{\Psi\rightarrow n}\left\{ \langle\Psi|\hat{T}|\Psi\rangle \right\} + E_{\text{Hxc}}[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) \right\} \\
&= \min_{n}\left\{ \min_{\Psi\rightarrow n}\left\{ \langle\Psi|\hat{T}|\Psi\rangle + E_{\text{Hxc}}[n_{\Psi}] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})n_{\Psi}(\mathbf{r}) \right\} \right\} \\
&= \min_{n}\left\{ \min_{\Psi\rightarrow n}\left\{ \langle\Psi|\hat{H}-\hat{W}_{\text{ee}}|\Psi\rangle + E_{\text{Hxc}}[n_{\Psi}] \right\} \right\} \\
&= \min_{\Psi}\left\{ \langle\Psi|\hat{H}-\hat{W}_{\text{ee}}|\Psi\rangle + E_{\text{Hxc}}[n_{\Psi}] \right\}
\end{aligned}
$$

Comparing variational principles

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

Comparing variational principles

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

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

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

↓

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

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

Comparing variational principles

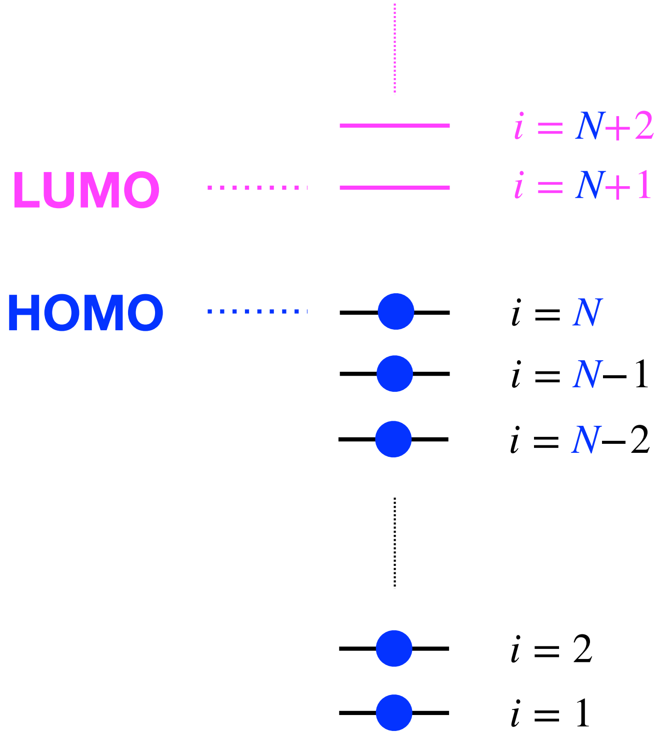
$$E_0 = \min_{\Psi}\left\{\langle\Psi|\hat{H}|\Psi\rangle\right\} = \boxed{\min_{\Psi}\left\{\langle\Psi|\hat{H}-\hat{W}_{\mathrm{ee}}|\Psi\rangle+E_{\mathrm{Hxc}}[n_{\Psi}]\right\}}$$

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

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

DFT for N-electron ground states

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



$i = N+2$

LUMO $i = N+1$

HOMO $i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$

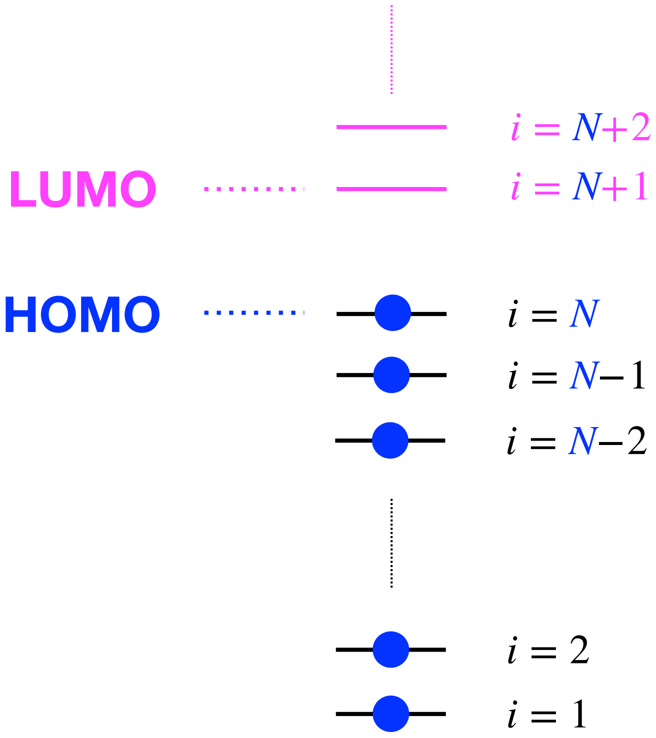
W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

DFT for N-electron ground states

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

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

exact ground-state
density



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

DFT for N-electron ground states

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

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

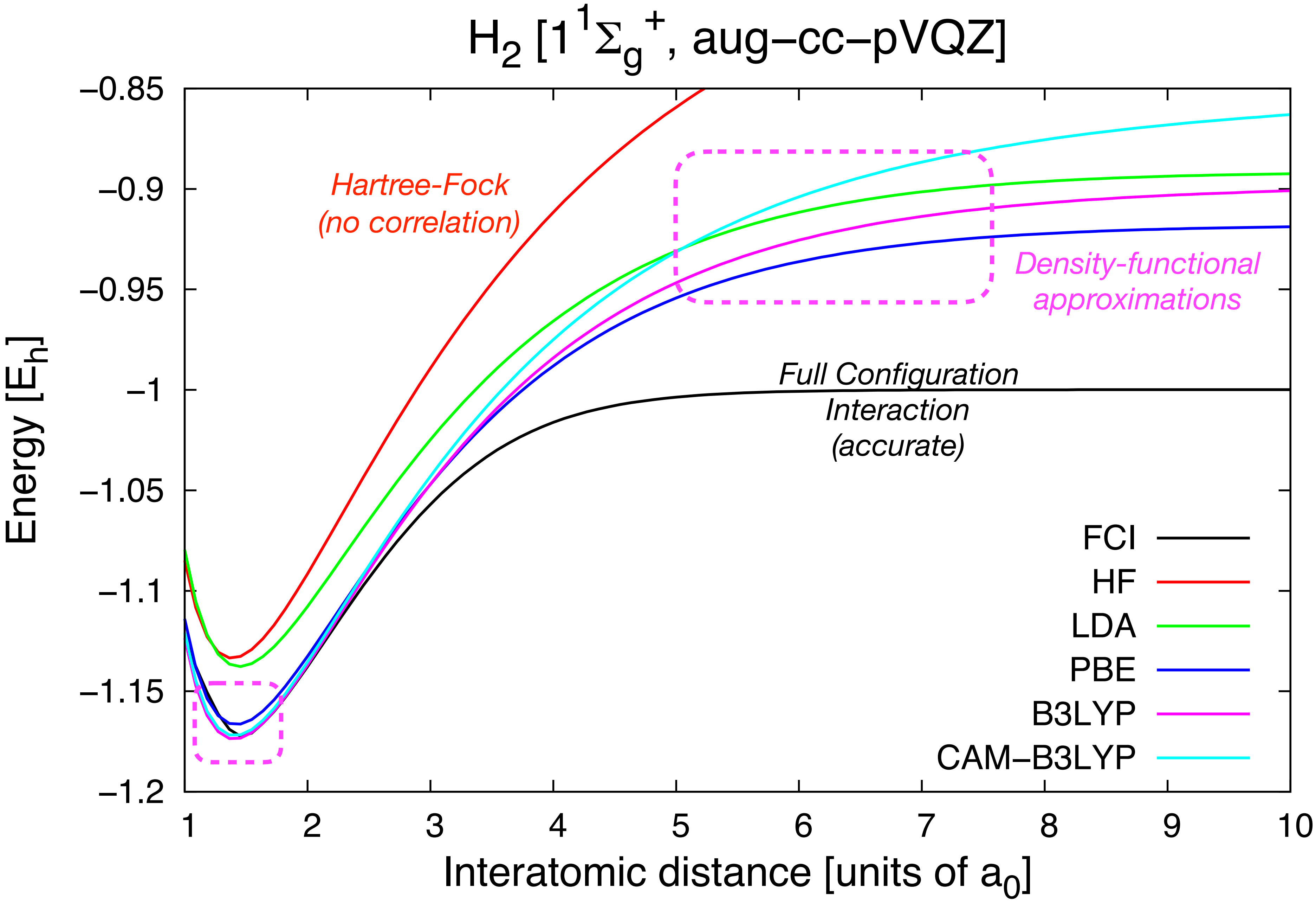
exact ground-state ***density***

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

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

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

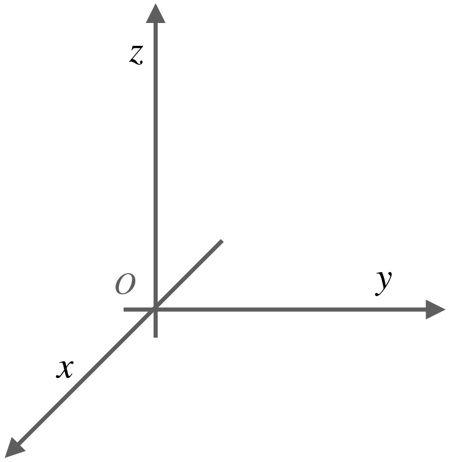
Success and failures of density-functional approximations



Prototypical hydrogen molecule

H **H**

Prototypical hydrogen molecule



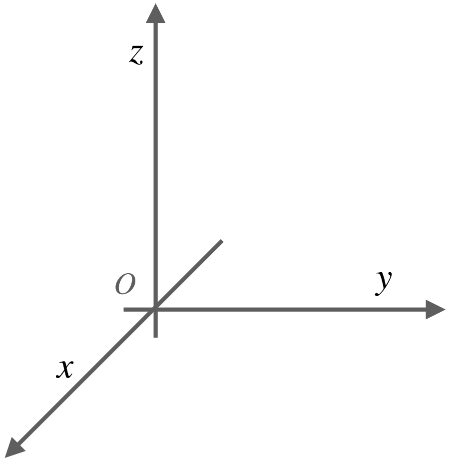
$\mathbf{R}_B \equiv (x_B, y_B, z_B)$

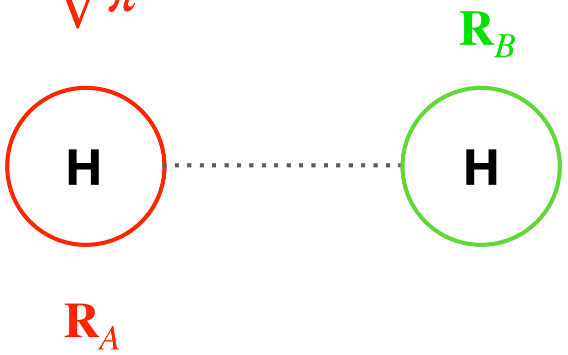
H ······················ **H**

$\mathbf{R}_A \equiv (x_A, y_A, z_A)$

Prototypical hydrogen molecule

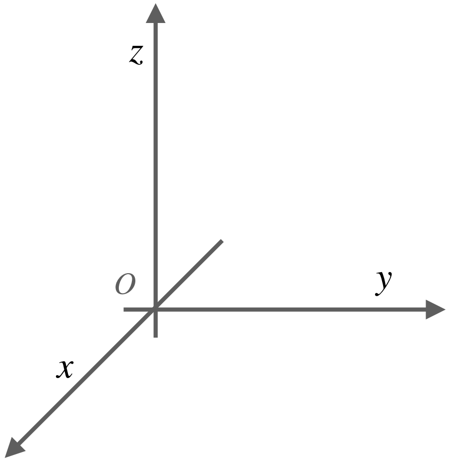
$$\chi_{s_A}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_A|}$$



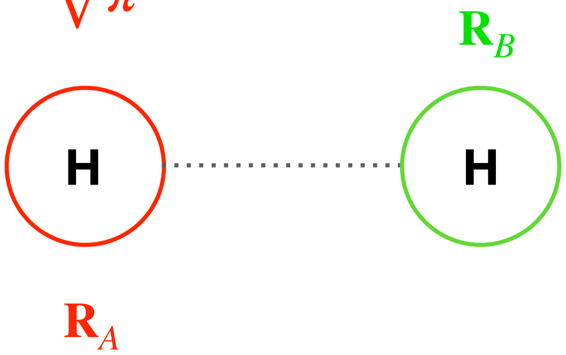


$$\chi_{s_B}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_B|}$$

Prototypical hydrogen molecule



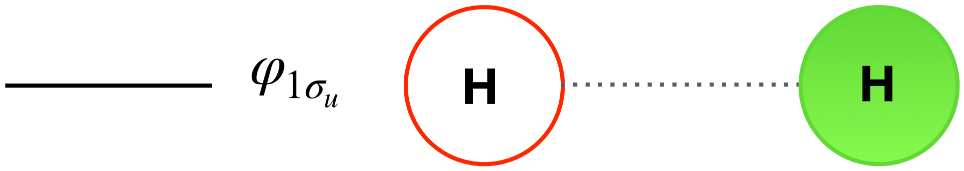
$$\chi_{s_A}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_A|}$$



$$\chi_{s_B}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_B|}$$

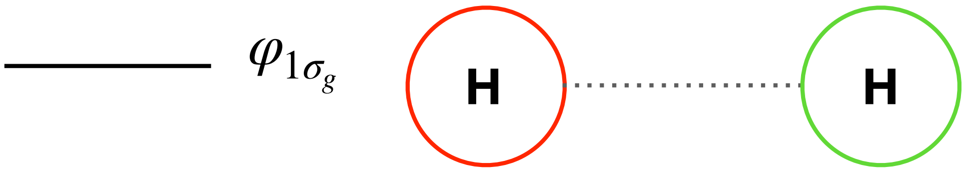
χ_{s_A} and χ_{s_B} are ***localised orbitals***

Prototypical hydrogen molecule



$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\right)$$

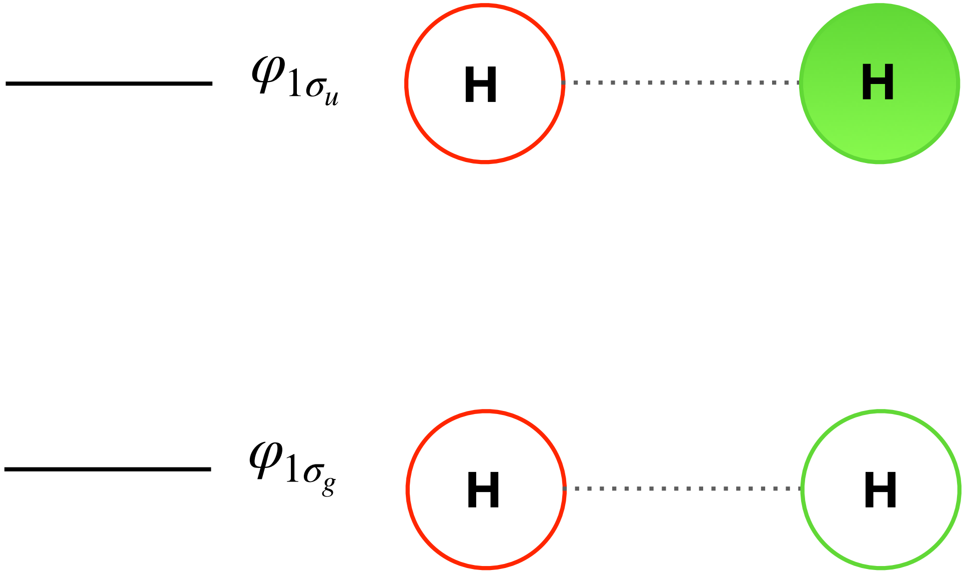
Anti-bonding orbital



$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)$$

Bonding orbital

Prototypical hydrogen molecule



$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\right)$$

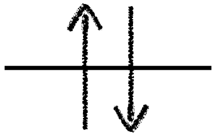
Anti-bonding orbital

$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)$$

Bonding orbital

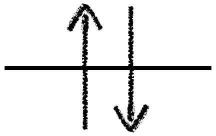
$\varphi_{1\sigma_g}$ *and* $\varphi_{1\sigma_u}$ *are* ***delocalised orbitals***

Single-configuration ground-state two-electron wave function



$\varphi_{1\sigma_g}$ $\quad\Leftrightarrow\quad$ $\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$

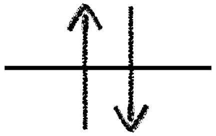
Single-configuration ground-state two-electron wave function



$\varphi_{1\sigma_g}$ $\Leftrightarrow$ $\boxed{\varphi_{1\sigma_g}}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$

$$\boxed{\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)}$$

Single-configuration ground-state two-electron wave function

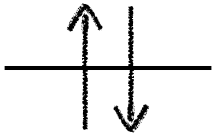


$\varphi_{1\sigma_g}$ ⇔ $\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$

$$\frac{1}{2}\Big(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\Big)$$

H ······· **H**   **H** ······· **H**   **H**$^-$·······**H**$^+$ **H**$^+$·······**H**$^-$

Single-configuration ground-state two-electron wave function



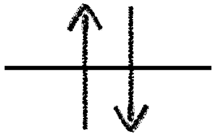
$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$

H ······· **H**   **H** ······· **H** $\mathbf{H}^-$·······$\mathbf{H}^+$ $\mathbf{H}^+$·······$\mathbf{H}^-$

Ionic configurations

Single-configuration ground-state two-electron wave function

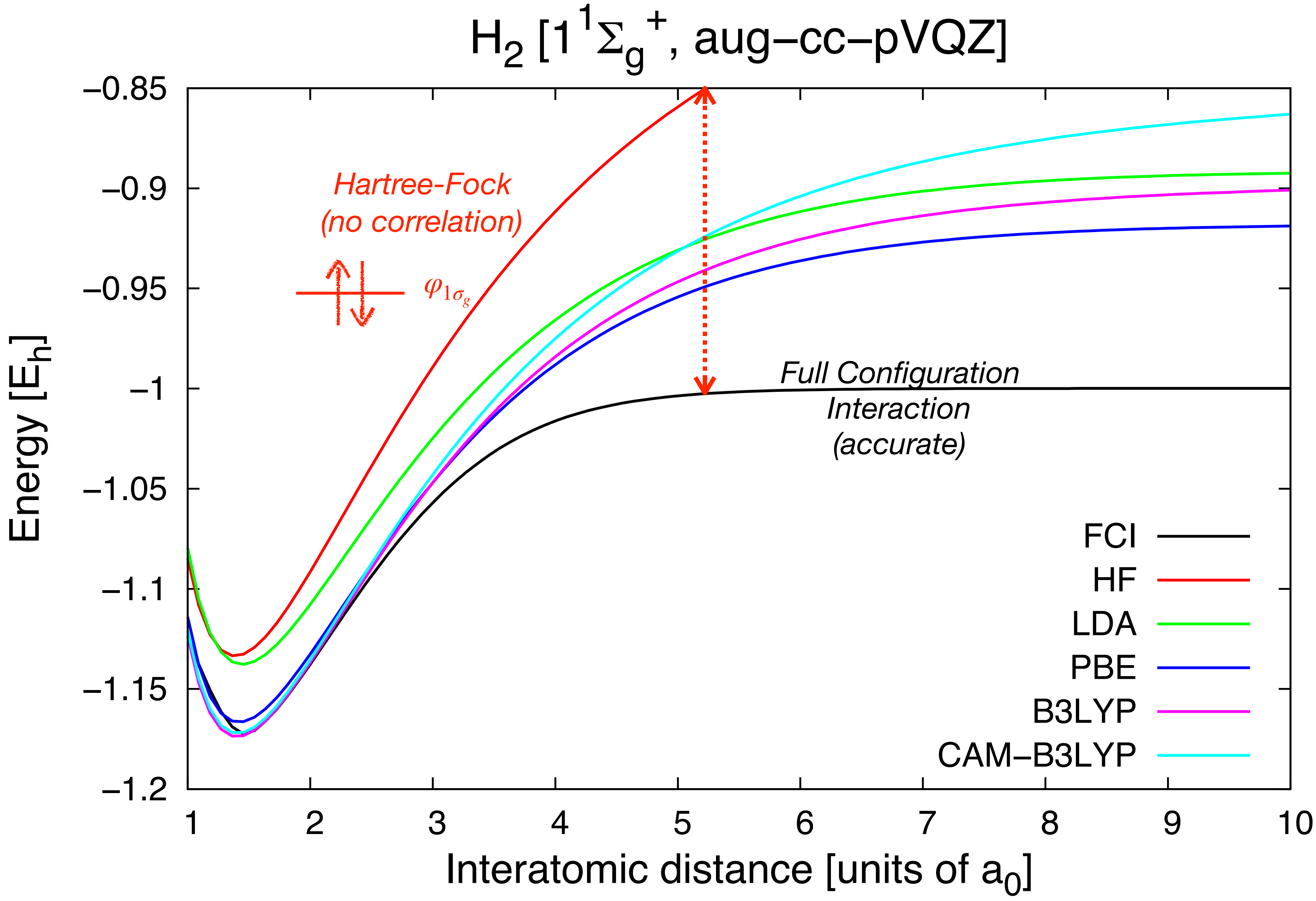


$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

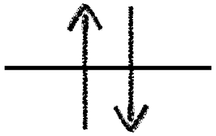
$$\frac{1}{2}\Big(\underset{\textbf{H}\cdots\cdots\textbf{H}}{\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)} + \underset{\textbf{H}\cdots\cdots\textbf{H}}{\chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)} + \boxed{\underset{\textbf{H}^-\cdots\cdots\textbf{H}^+}{\chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2)} + \underset{\textbf{H}^+\cdots\cdots\textbf{H}^-}{\chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)}}\Big)$$

Ionic configurations

Unphysical *in the dissociation limit!*


H_2 [$1^1\Sigma_g^+$, aug–cc–pVQZ]
–0.85
–0.9
–0.95
–1
–1.05
–1.1
–1.15
–1.2
Energy [E_h]
1
2
3
4
5
6
7
8
9
10
Interatomic distance [units of a_0]
Hartree-Fock
(no correlation)
$\varphi_{1\sigma_g}$
Full Configuration
Interaction
(accurate)
FCI
HF
LDA
PBE
B3LYP
CAM–B3LYP

Single-configuration ground-state two-electron wave function



$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

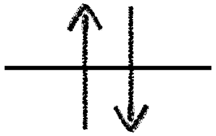
$$\frac{1}{2}\Big(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\Big)$$

H .... **H** **H** .... **H** $\mathbf{H}^{-}$ .... $\mathbf{H}^{+}$ $\mathbf{H}^{+}$ .... $\mathbf{H}^{-}$

Electron density *in the dissociation limit*

$$2\left|\varphi_{1\sigma_g}(\mathbf{r})\right|^2 = 2\varphi_{1\sigma_g}(\mathbf{r})\varphi_{1\sigma_g}(\mathbf{r}) = \left|\chi_{s_A}(\mathbf{r})\right|^2 + \left|\chi_{s_B}(\mathbf{r})\right|^2 + 2\chi_{s_A}(\mathbf{r})\chi_{s_B}(\mathbf{r})$$

Single-configuration ground-state two-electron wave function

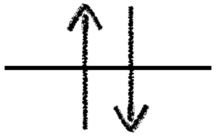


$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

Electron density in the ***dissociation limit***

$$2\left|\varphi_{1\sigma_g}(\mathbf{r})\right|^2 = 2\varphi_{1\sigma_g}(\mathbf{r})\varphi_{1\sigma_g}(\mathbf{r}) = \left|\chi_{s_A}(\mathbf{r})\right|^2 + \left|\chi_{s_B}(\mathbf{r})\right|^2 + 2\overbrace{\chi_{s_A}(\mathbf{r})\chi_{s_B}(\mathbf{r})}^{\approx 0}$$

Single-configuration ground-state two-electron wave function



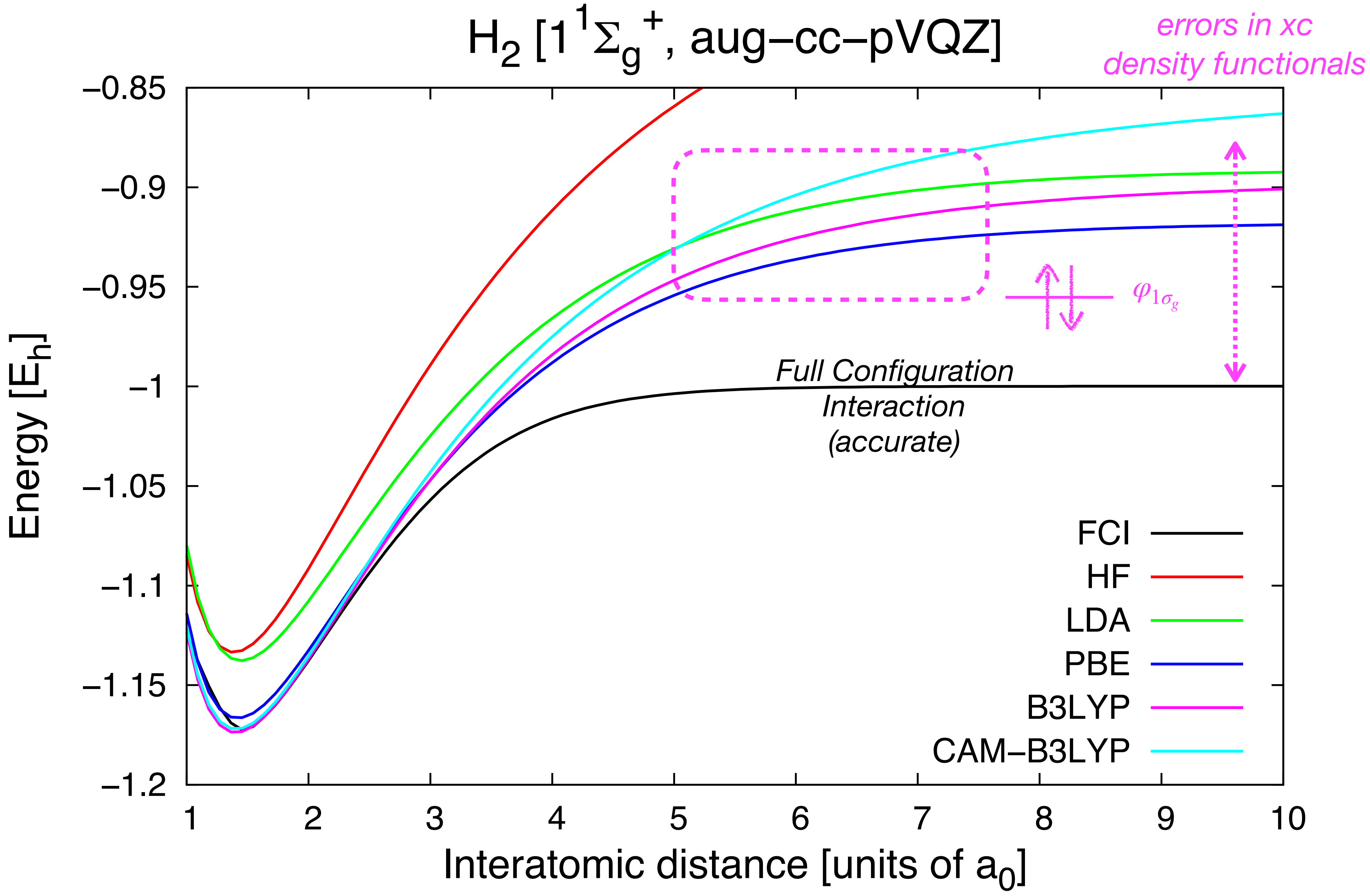
$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

density *of the first hydrogen atom*

density *of the second hydrogen atom*

$$2\left|\varphi_{1\sigma_g}(\mathbf{r})\right|^2 = 2\varphi_{1\sigma_g}(\mathbf{r})\varphi_{1\sigma_g}(\mathbf{r}) \approx \left|\chi_{s_A}(\mathbf{r})\right|^2 + \left|\chi_{s_B}(\mathbf{r})\right|^2$$

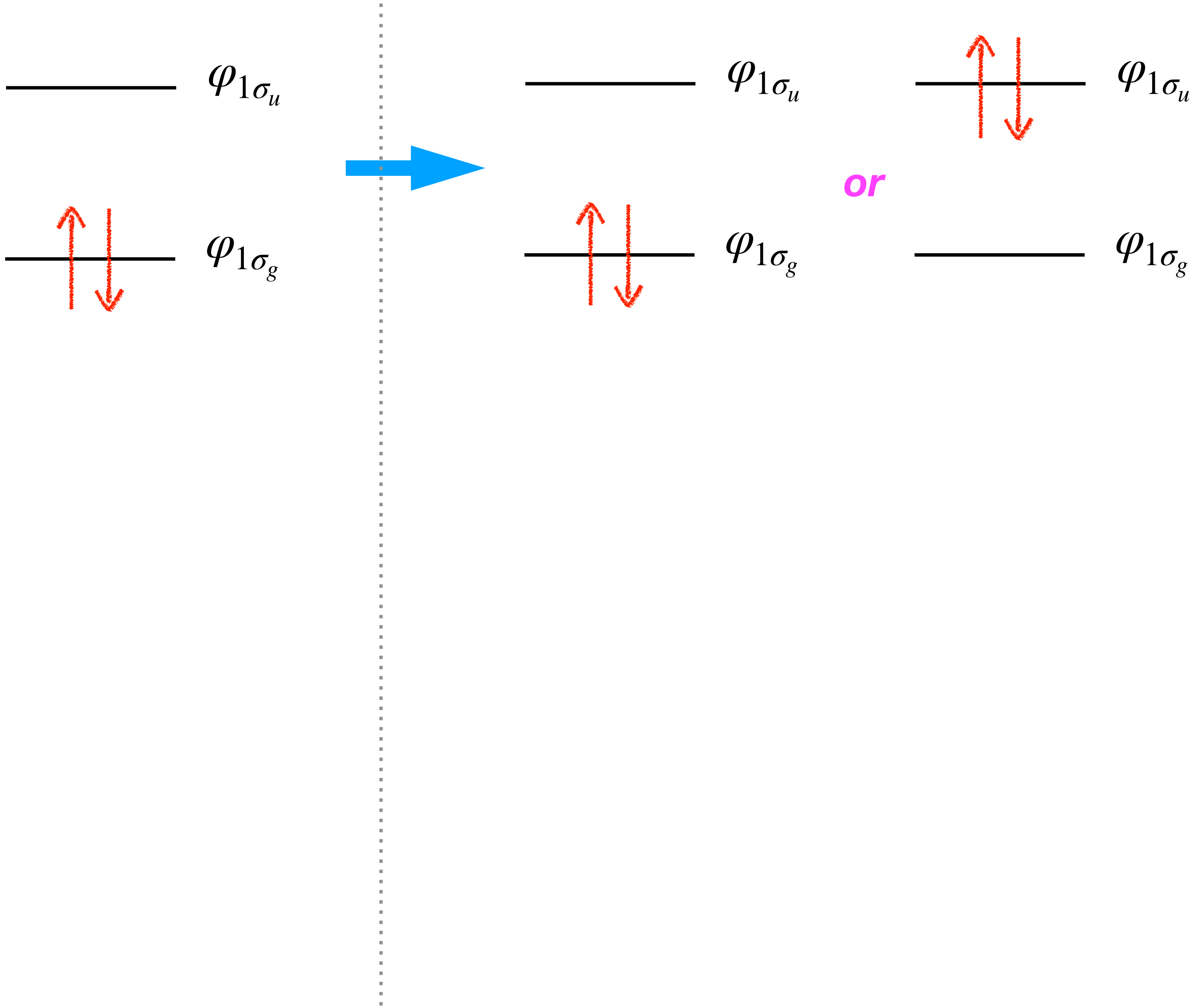
✓



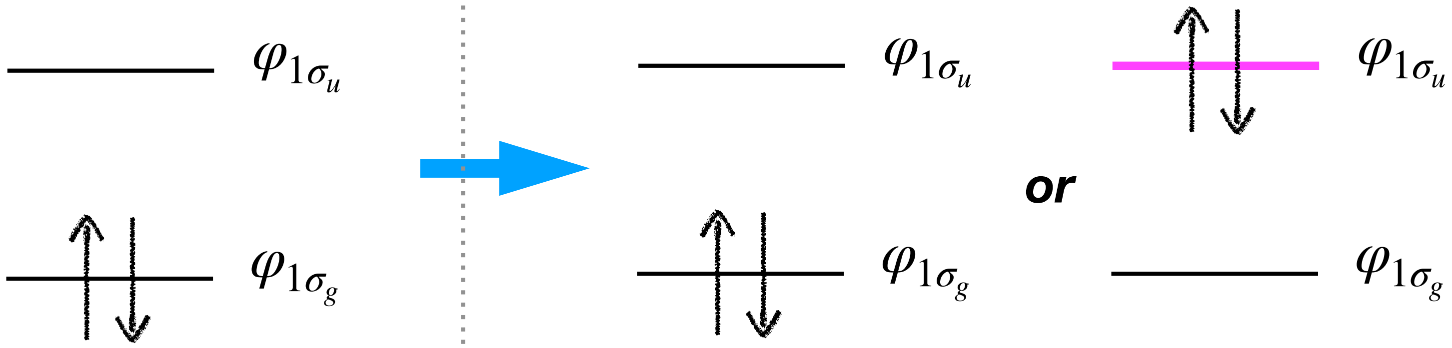
errors in xc density functionals

Full Configuration Interaction (accurate)

Multi-configurational wave function

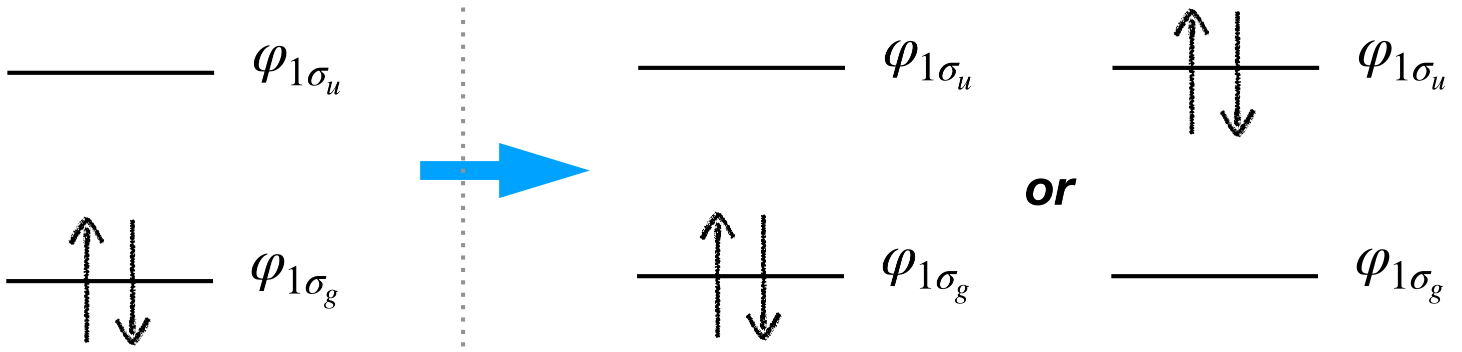


Multi-configurational wave function



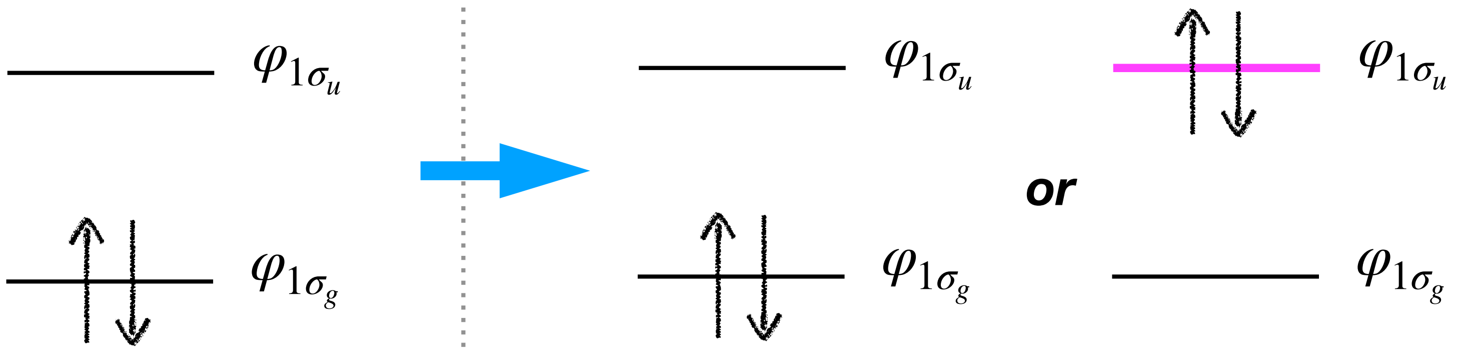
$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)-\varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

Multi-configurational wave function



$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) \overset{\substack{\textbf{minus}\text{ combination}\\ \downarrow}}{-} \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

Multi-configurational wave function

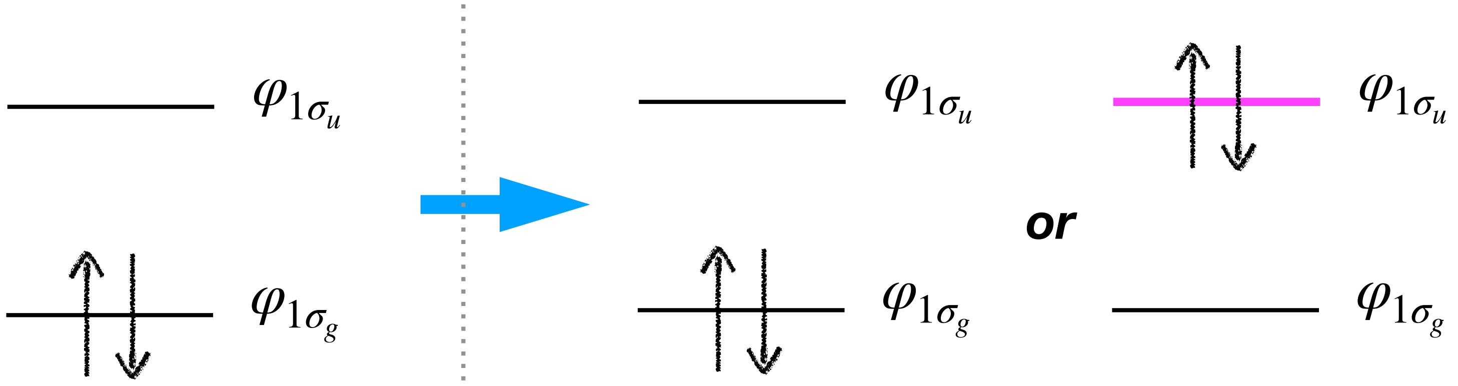


$$\boxed{\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\Big(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\Big)}$$

$$\equiv \frac{1}{\sqrt{2}}\Big(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\Big)$$

$$\boxed{\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\Big(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\Big)}$$

Multi-configurational wave function

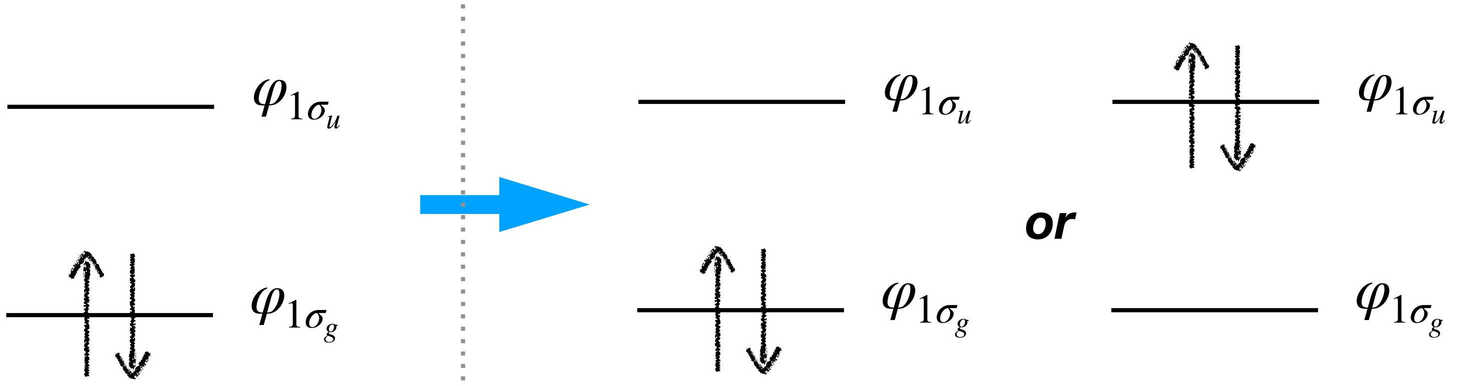


$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)-\varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

H .... **H** **H** .... **H**

Multi-configurational wave function



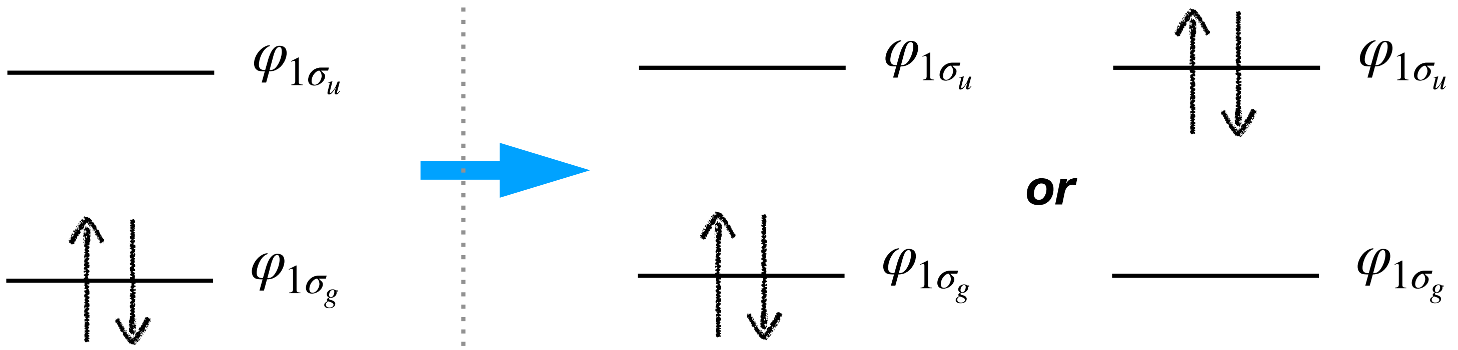
$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

Localised *picture* →

$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

H ……. **H** **H** ……. **H**

Multi-configurational wave function



$$\equiv \frac{1}{\sqrt{2}}\Big(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\Big)$$

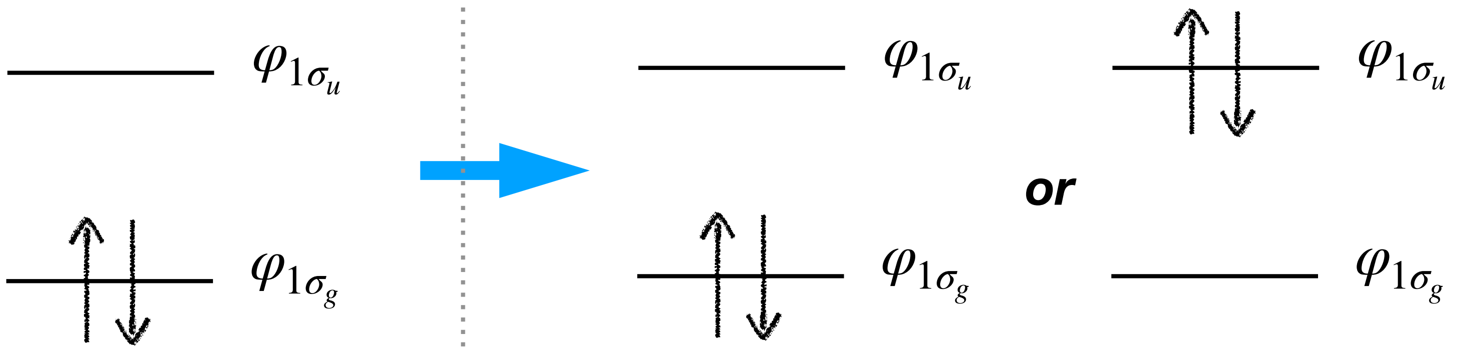
***Localised** picture*

$$= \frac{1}{\sqrt{2}}\Big(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\Big)$$

H .... **H** **H** .... **H**

Strong electron correlation

Multi-configurational wave function

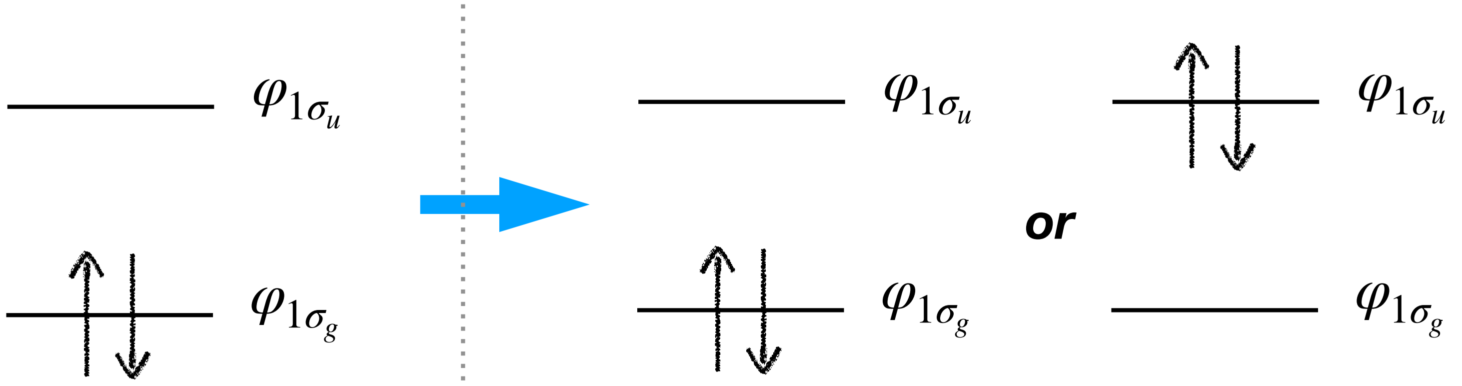


***Delocalised** picture* →

$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

$$= \frac{1}{\sqrt{2}}\left(\underbrace{\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)}_{\mathbf{H}\cdots\cdots\mathbf{H}} + \underbrace{\chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)}_{\mathbf{H}\cdots\cdots\mathbf{H}}\right)$$

Multi-configurational wave function



***Delocalised** picture* ⟶

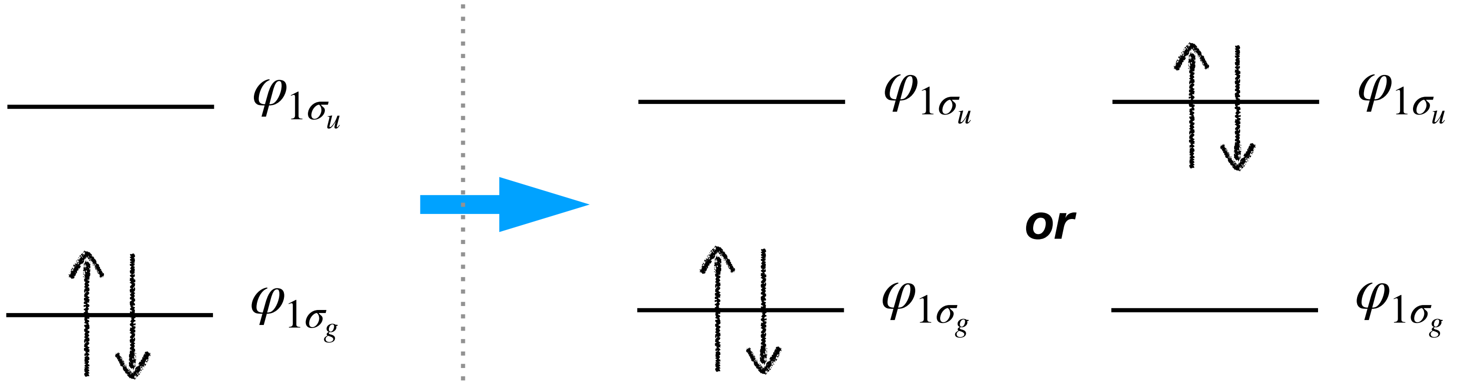
$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

Strong multi-configurational
character of the electronic structure

$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

H .... **H** **H** .... **H**

Multi-configurational wave function



***Delocalised** picture* →

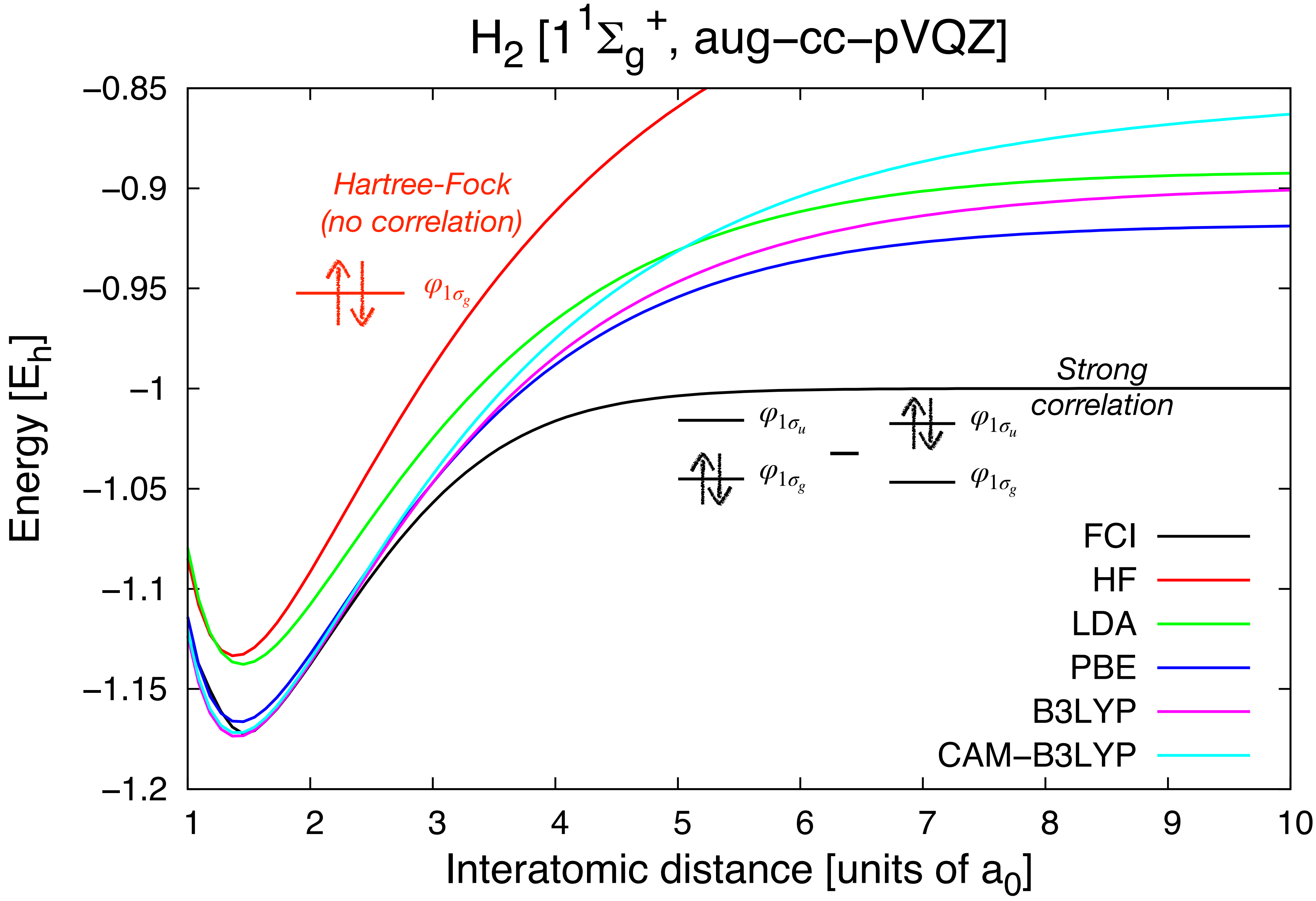
$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

Strong multi-configurational
character of the electronic structure

$$= \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1)\right)$$

H .... **H**   **H** .... **H**

correlation effect


H_2 [$1^1\Sigma_g^+$, aug–cc–pVQZ]
Energy [E_h]
Interatomic distance [units of a_0]
–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
Hartree-Fock
(no correlation)
$\varphi_{1\sigma_g}$
Strong
correlation
$\varphi_{1\sigma_u}$
$\varphi_{1\sigma_g}$
$\varphi_{1\sigma_u}$
$\varphi_{1\sigma_g}$
FCI
HF
LDA
PBE
B3LYP
CAM–B3LYP