Quantum embedding in electronic structure theory

Part 1: The electronic structure problem in Chemistry

Emmanuel Fromager

Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg,
Université de Strasbourg, Strasbourg, France.

Outline

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

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

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

Electronic Schrödinger equation

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

Electronic Schrödinger equation

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Electronic Hamiltonian
operator

Electronic Schrödinger equation

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Electronic Hamiltonian
operator

known!

Electronic Schrödinger equation

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

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

Electronic Schrödinger equation

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

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

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

Ground-state electronic
wave function

Electronic Schrödinger equation

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

Ground-state electronic
wave function

unknown!

N-electron wave function

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

electronic ***coordinates***

N-electron wave function

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

electronic ***coordinates***

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

Cartesian ***space*** *coordinates*

Spin *coordinate*

$$\mathbf{r}_i \equiv (x_i, y_i, z_i) \qquad \sigma_i = \uparrow \textbf{ or } \downarrow$$

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**

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

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

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)*

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

***One-electron local** (multiplicative) operator*

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

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*Kinetic energy+**nuclear attraction***

Electronic repulsion

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

not universal!

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

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

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

"external" potential energy

Electronic repulsion

N-electron Hamiltonian *(in atomic units)*

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

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

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)*

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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

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

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

Kinetic energy+nuclear attraction

***Two-electron local** (multiplicative) operator*

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

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

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

Kinetic energy+nuclear attraction

universal!

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

Electronic repulsion

N-electron ground-state Schrödinger equation

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

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

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

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

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

N-electron ground-state Schrödinger equation

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

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

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

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

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

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

… 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

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

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Minimisation *over*

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

Rayleigh-Ritz variational principle

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Minimisation over

*trial **normalised** wave functions* Ψ

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

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

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

Energy expectation value

for the trial wave function Ψ

Rayleigh-Ritz variational principle

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

Energy expectation value

for the trial wave function Ψ

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

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

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

Density-functional theory (DFT)

The Nobel Prize in Chemistry 1998

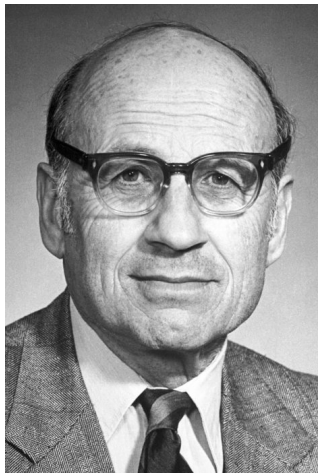
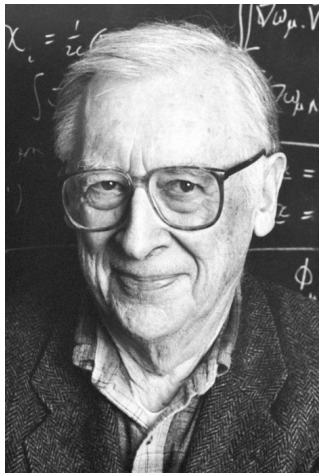


Photo from the Nobel Foundation archive.

Walter Kohn

Prize share: 1/2



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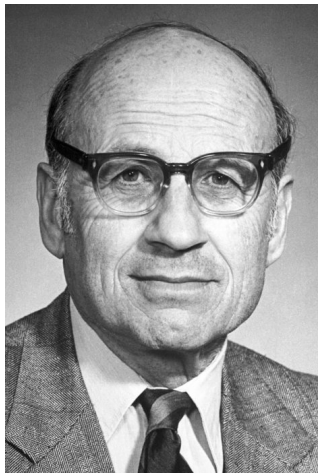
Prize share: 1/2

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 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."

The Nobel Prize in Chemistry 1998



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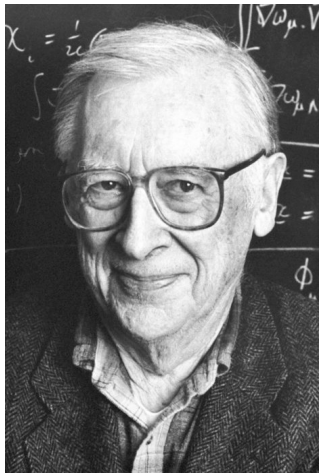

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John A. Pople
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It is ***in principle unnecessary to know*** the ground-state many-electron ***wave function*** Ψ_0 for evaluating the exact ground-state energy E_0.

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

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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

Electron density

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Density *of the many-electron wave function* Ψ

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

Electron density

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

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

Electron density

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

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

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

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

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

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

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

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

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

We do not need to know Ψ_0

Exact external potential energy

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We just need to know n_0

Exact external potential energy

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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

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

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

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

Levy's constrained search formalism

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

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

Minimisation over ***densities*** n

Levy's constrained search formalism

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

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

Ψ_4 Ψ_1 Ψ_2' Ψ_1'

Ψ_1'' Ψ_2

Ψ_3'' Ψ_2'' Ψ_3

Ψ_3' Ψ_5 Ψ_4''

Space of N-electron wave functions

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

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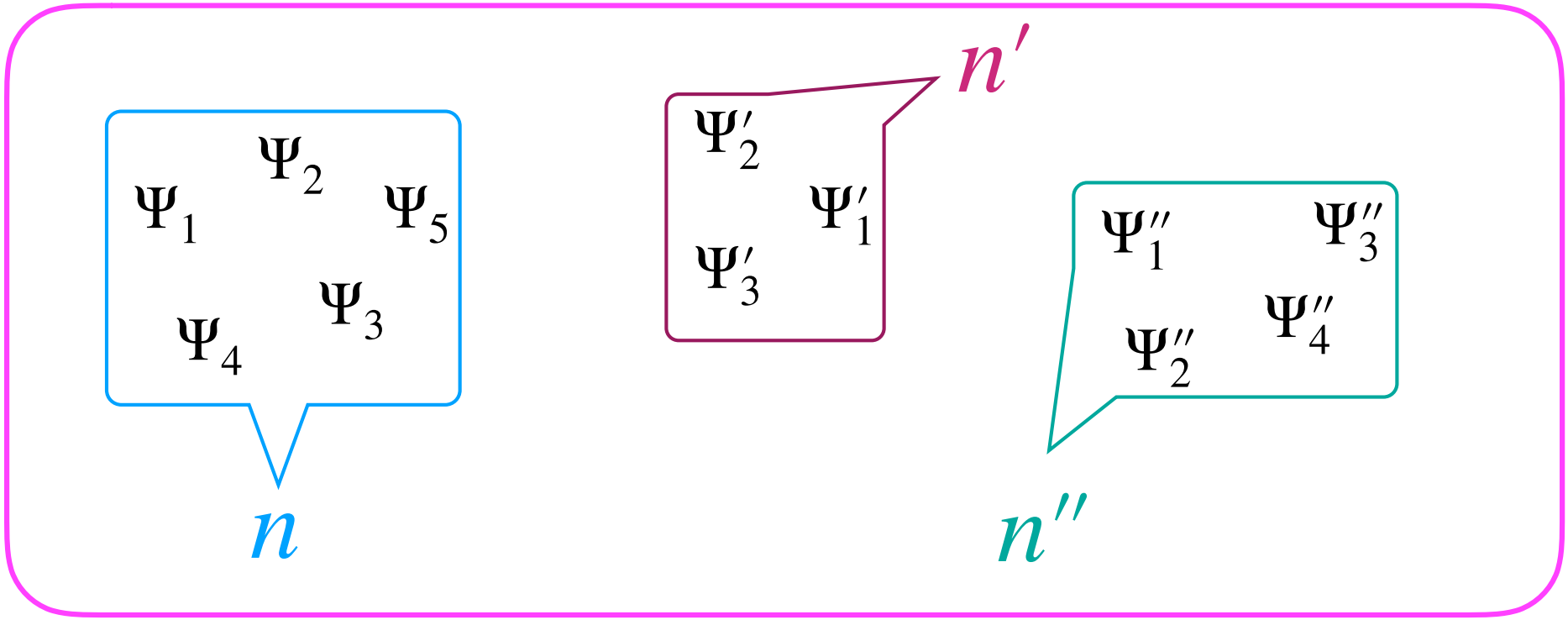

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Levy's constrained search formalism

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

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

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

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

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

Levy's constrained search formalism

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

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

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Levy's constrained search formalism

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

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

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

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

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

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

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

Kohn-Sham

$$\longrightarrow$$

$$T_{\mathrm{s}}[n] = \min_{\Psi \to n} \langle \Psi \,|\, \hat{T} \,|\, \Psi \rangle$$

Interacting universal functional

Non-interacting
(kinetic energy) functional

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

Kohn-Sham DFT formalism

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

Interacting universal functional

Non-interacting
(kinetic energy) functional

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

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

Kohn-Sham DFT formalism

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

Interacting universal functional

Non-interacting
(kinetic energy) functional

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

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

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)

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

Kohn-Sham DFT formalism

***Hartree** density functional*

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

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

***Exchange-correlation (xc)** density functional*

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

← ***Quantum***
many-electron effects

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

Variational principle in Kohn-Sham DFT

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

$$= \min_n \left\{ T_{\text{s}}[n] + E_{\text{Hxc}}[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \right\}$$

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

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

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

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

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

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

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

Comparing variational principles

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

Kohn-Sham DFT

Comparing variational principles

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

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

Comparing variational principles

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

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

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

Comparing variational principles

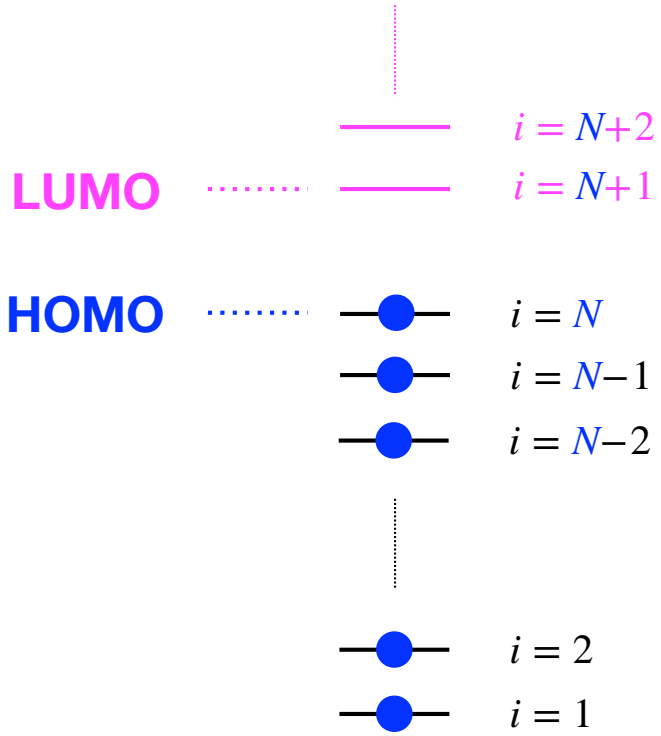
$$E_0 = \min_{\Psi} \left\{ \langle \Psi | \hat{H} | \Psi \rangle \right\} = \min_{\Psi} \left\{ \langle \Psi | \hat{H} - \hat{W}_{ee} | \Psi \rangle + E_{Hxc}[n_\Psi] \right\}$$

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

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



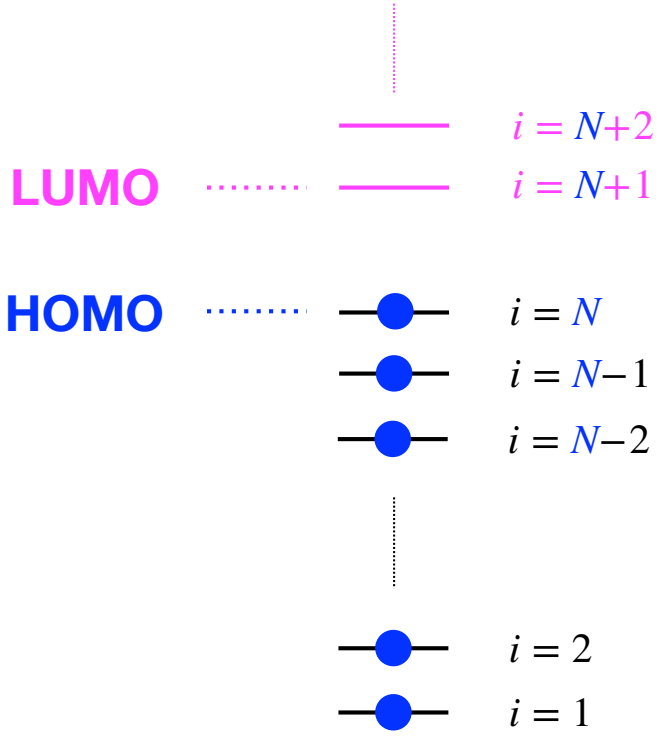
W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

DFT for N-electron ground states

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

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

exact ground-state ***density***



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

DFT for N-electron ground states

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

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

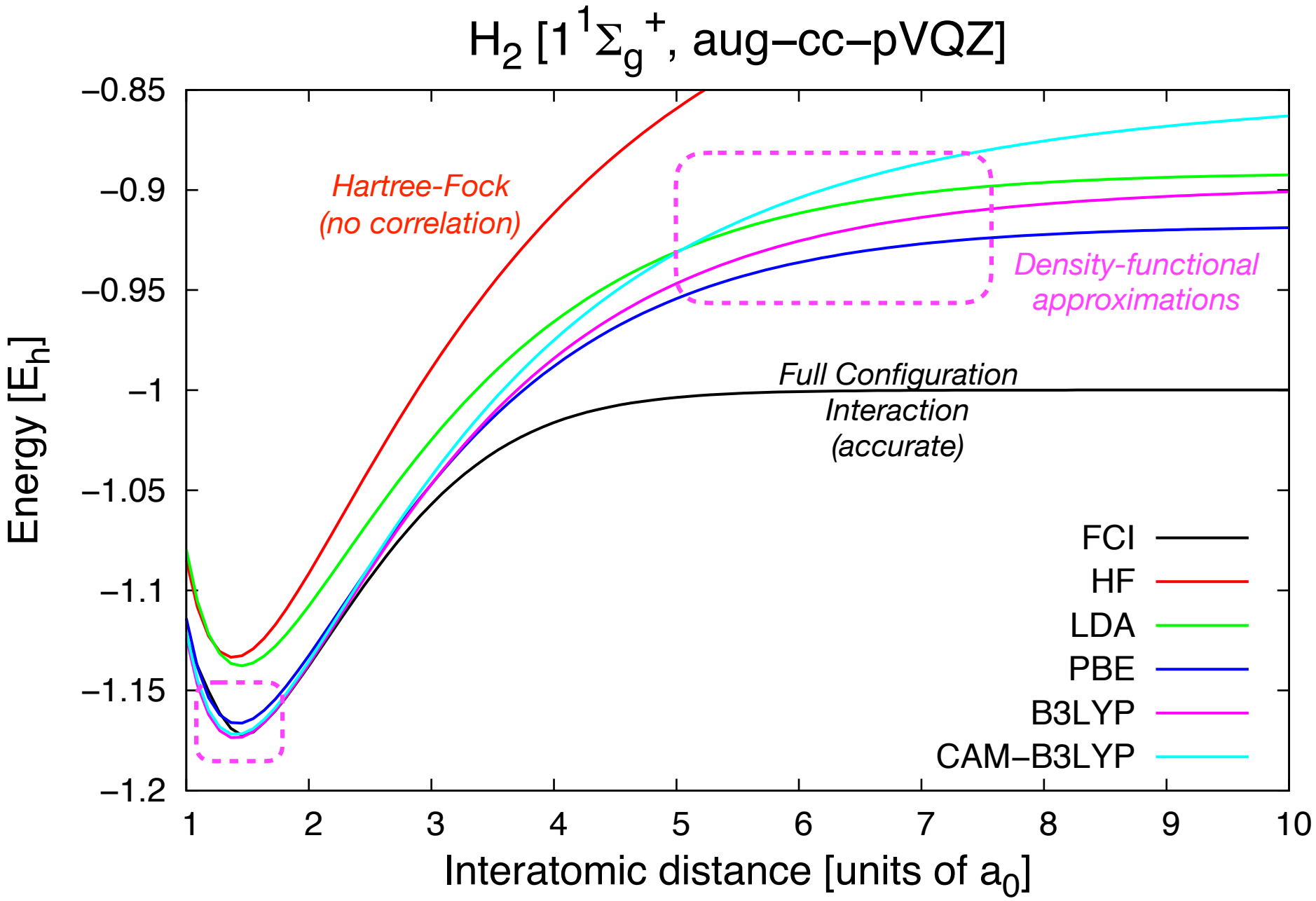
exact ground-state ***density***

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

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

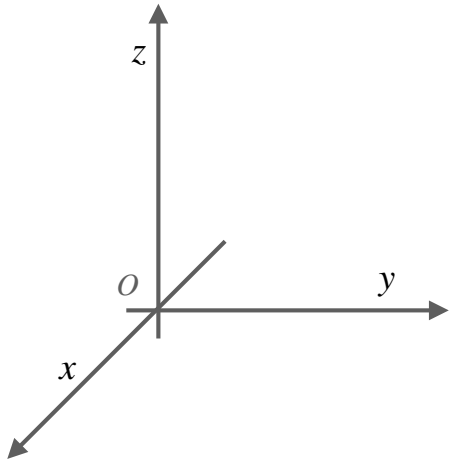
W. Kohn and L. J. Sham, Phys. Rev. A 140, 1133 (1965).

Success and failures of density-functional approximations



Prototypical hydrogen molecule

Prototypical hydrogen molecule

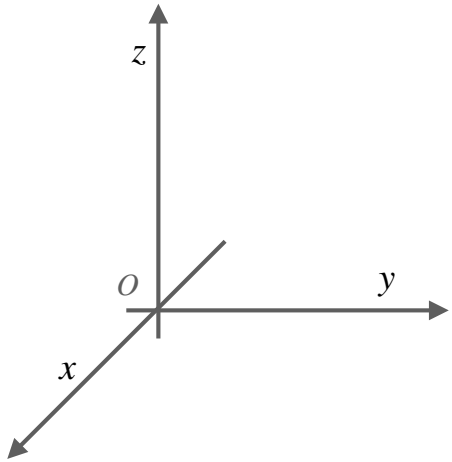


$\mathbf{R}_B \equiv (x_B, y_B, z_B)$

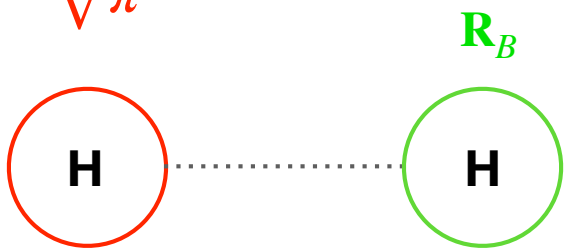
H ..... H

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

Prototypical hydrogen molecule

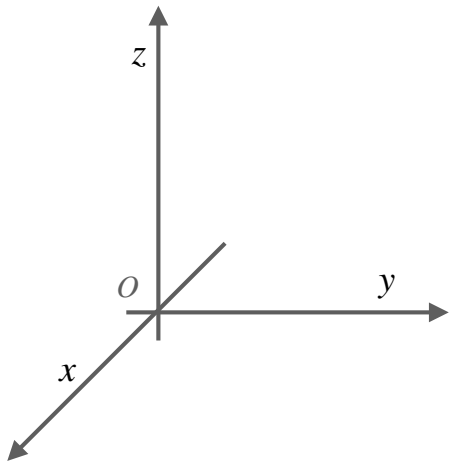


$$\chi_{s_A}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_A|}$$

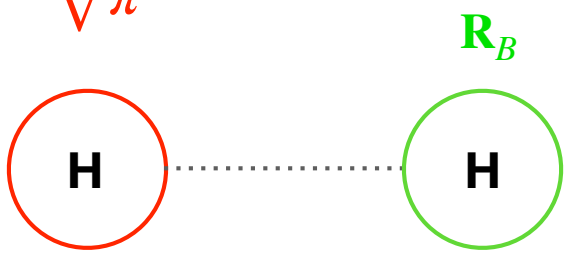


$$\chi_{s_B}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_B|}$$

Prototypical hydrogen molecule



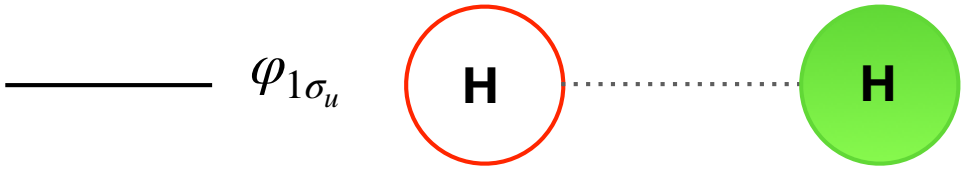
$$\chi_{s_A}(\mathbf{r}) = \frac{1}{\sqrt{\pi}} e^{-|\mathbf{r}-\mathbf{R}_A|}$$



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

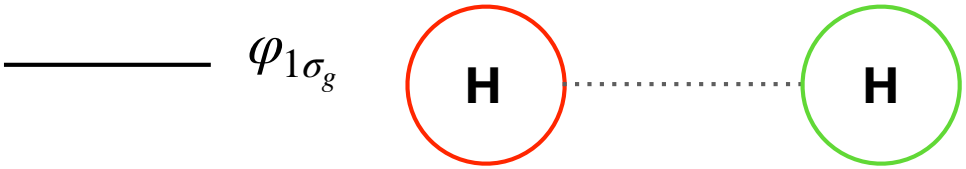
χ_{s_A} *and* χ_{s_B} *are* ***localised orbitals***

Prototypical hydrogen molecule



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

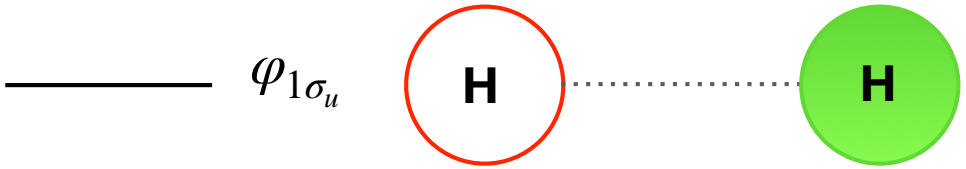
Anti-bonding orbital



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

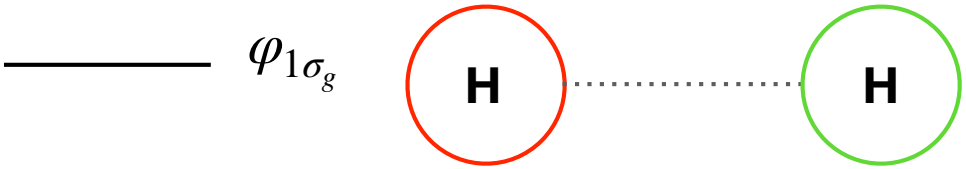
Bonding orbital

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

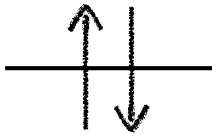


$$\varphi_{1\sigma_g}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) + \chi_{s_B}(\mathbf{r})\right)$$

Bonding orbital

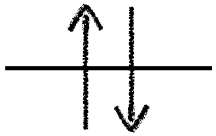
$\varphi_{1\sigma_g}$ *and* $\varphi_{1\sigma_u}$ *are* ***delocalised orbitals***

Single-configuration ground-state two-electron wave function



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

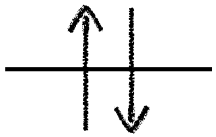
Single-configuration ground-state two-electron wave function



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

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

Single-configuration ground-state two-electron wave function

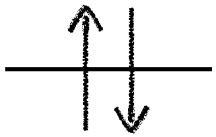


$\varphi_{1\sigma_g}$ $\Leftrightarrow$ $\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$

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

H ..... H H ..... H H^- ..... H^+ H^+ ..... H^-

Single-configuration ground-state two-electron wave function



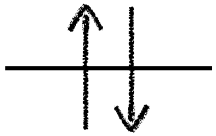
$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

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

$\mathrm{H}\cdots\mathrm{H}$ $\mathrm{H}\cdots\mathrm{H}$ $\mathrm{H}^-\cdots\mathrm{H}^+$ $\mathrm{H}^+\cdots\mathrm{H}^-$

Ionic configurations

Single-configuration ground-state two-electron wave function



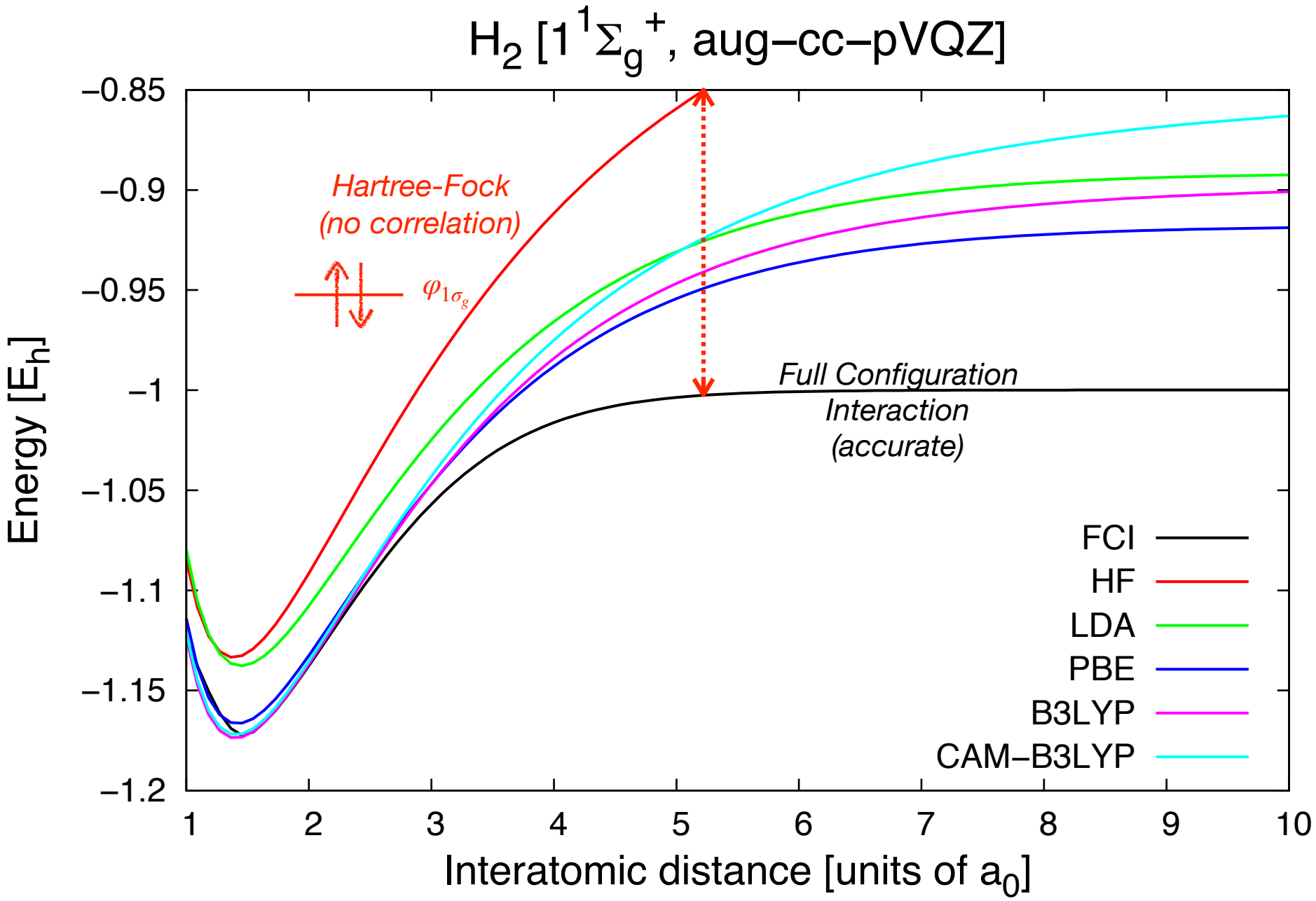
$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

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

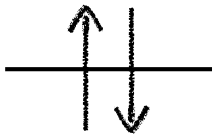
$\mathrm{H}\cdots\mathrm{H}$ $\quad$ $\mathrm{H}\cdots\mathrm{H}$ $\quad$ $\mathrm{H}^-\cdots\mathrm{H}^+$ $\quad$ $\mathrm{H}^+\cdots\mathrm{H}^-$

Ionic configurations

Unphysical *in the dissociation limit!*


H2 [1 1Σg+, aug–cc–pVQZ]
Energy [Eh]
Interatomic distance [units of a0]
–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)
φ1σg
Full Configuration
Interaction
(accurate)
FCI
HF
LDA
PBE
B3LYP
CAM–B3LYP

Single-configuration ground-state two-electron wave function



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

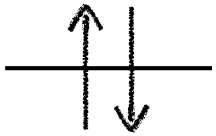
$$\frac{1}{2}\left(\chi_{s_A}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2) + \chi_{s_A}(\mathbf{r}_2)\chi_{s_B}(\mathbf{r}_1) + \chi_{s_A}(\mathbf{r}_1)\chi_{s_A}(\mathbf{r}_2) + \chi_{s_B}(\mathbf{r}_1)\chi_{s_B}(\mathbf{r}_2)\right)$$

$\mathbf{H}\cdots\mathbf{H}$ $\quad$ $\mathbf{H}\cdots\mathbf{H}$ $\quad$ $\mathbf{H}^-\cdots\mathbf{H}^+$ $\quad$ $\mathbf{H}^+\cdots\mathbf{H}^-$

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

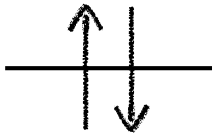


$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

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

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

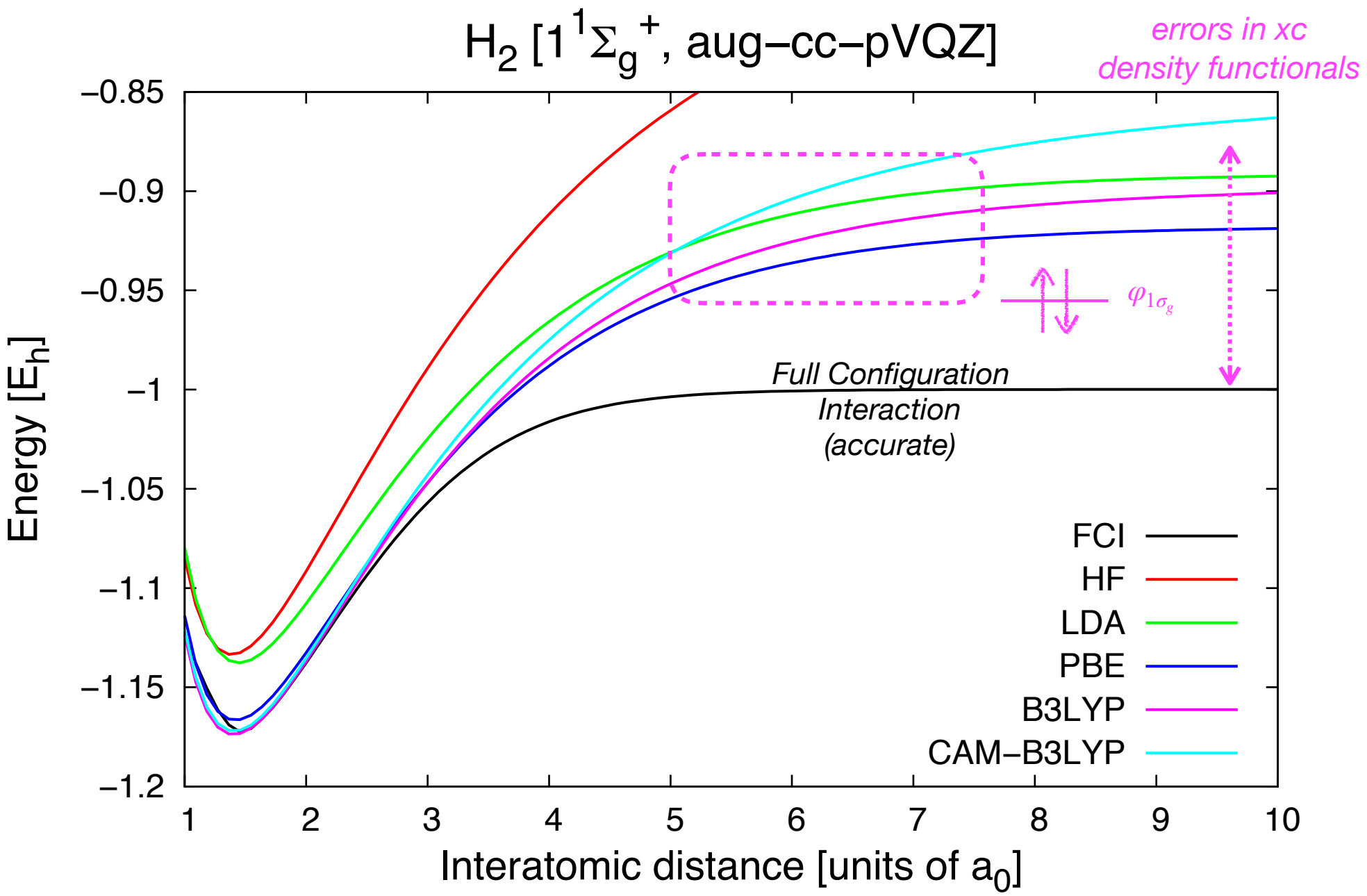
Single-configuration ground-state two-electron wave function



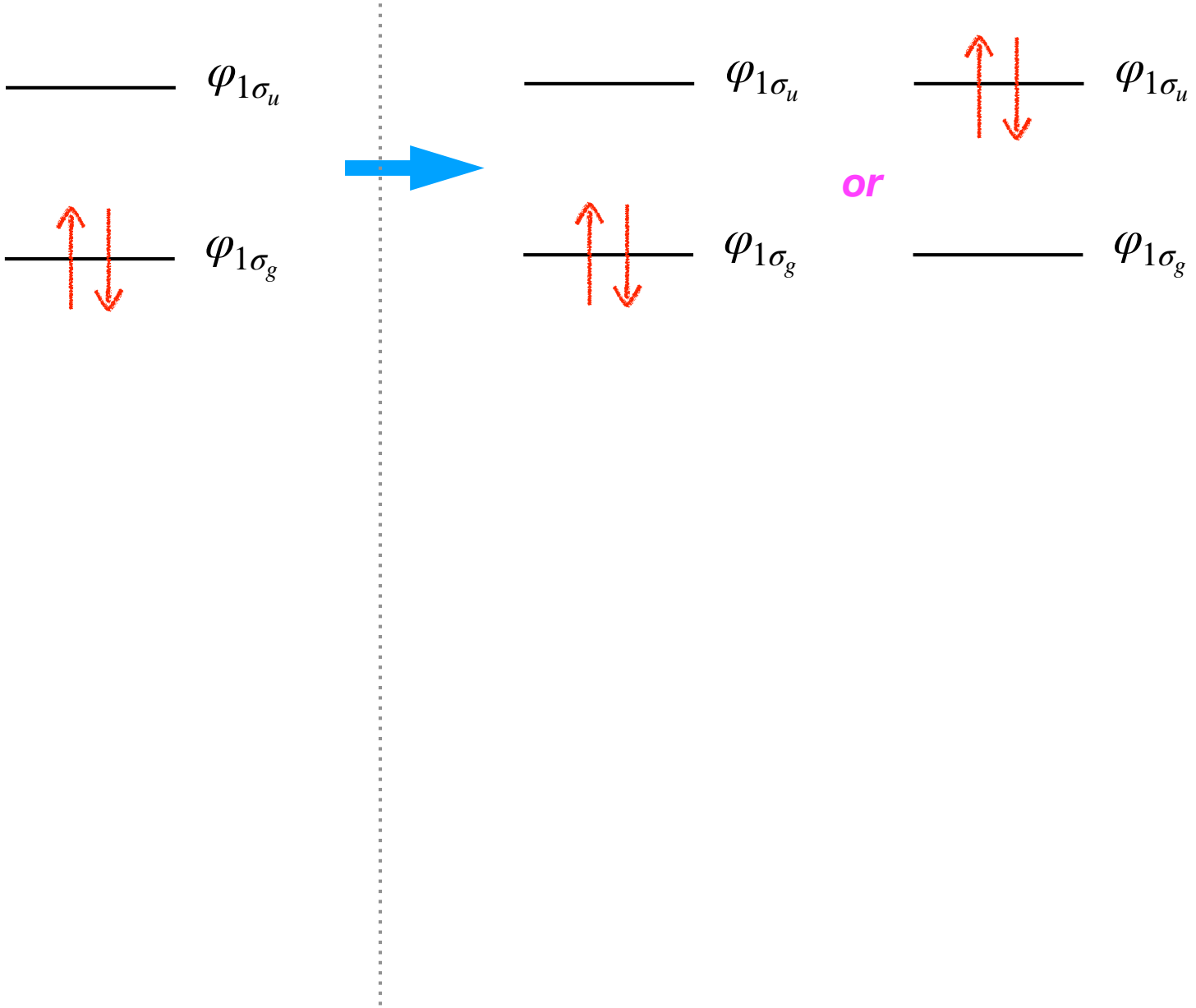
$$\varphi_{1\sigma_g} \quad \Leftrightarrow \quad \varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2)$$

__density__ of the first hydrogen atom *__density__ of the second hydrogen atom*

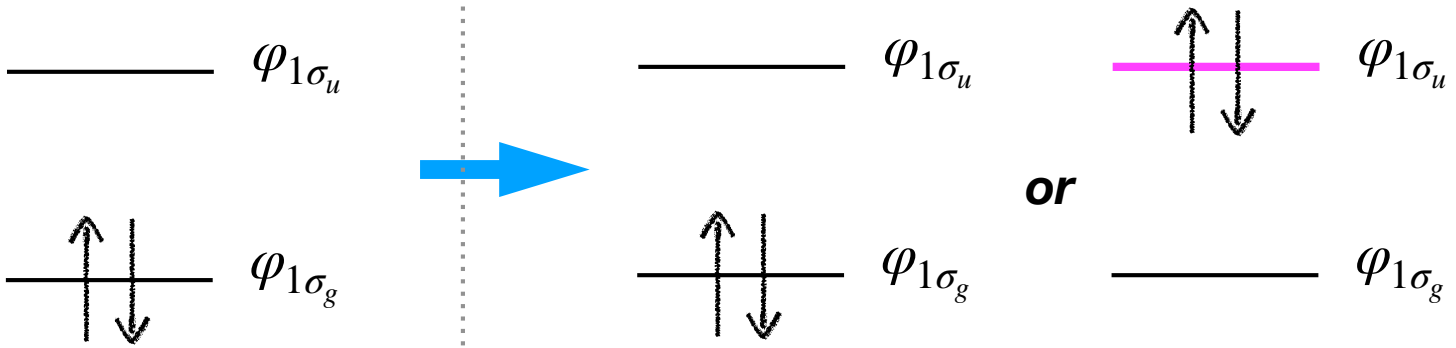
$$2\left|\varphi_{1\sigma_g}(\mathbf{r})\right|^2 = 2\varphi_{1\sigma_g}(\mathbf{r})\varphi_{1\sigma_g}(\mathbf{r}) \approx \left|\chi_{s_A}(\mathbf{r})\right|^2 + \left|\chi_{s_B}(\mathbf{r})\right|^2$$


H2 [1 1Σg+, aug–cc–pVQZ]
errors in xc
density functionals
Energy [Eh]
Interatomic distance [units of a0]
Full Configuration
Interaction
(accurate)
φ1σg
FCI
HF
LDA
PBE
B3LYP
CAM–B3LYP
–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

Multi-configurational wave function

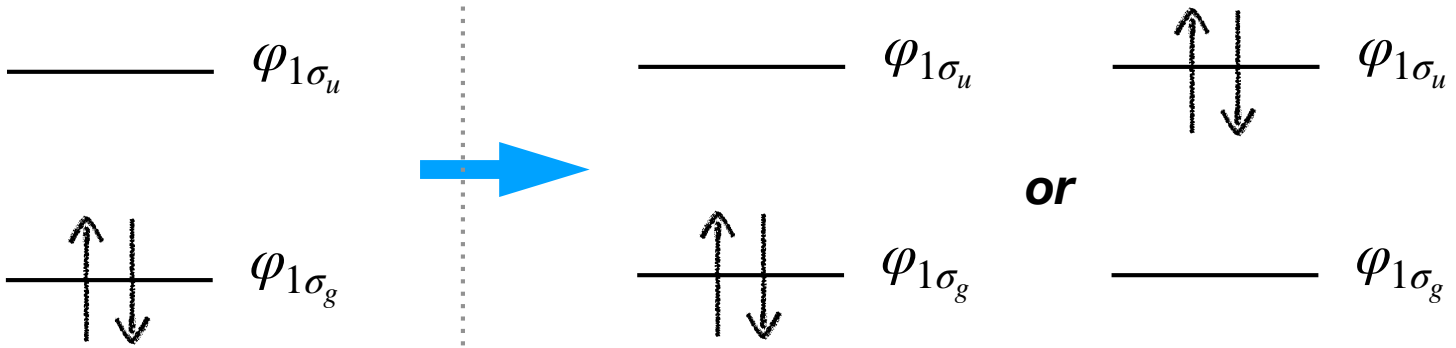


Multi-configurational wave function



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

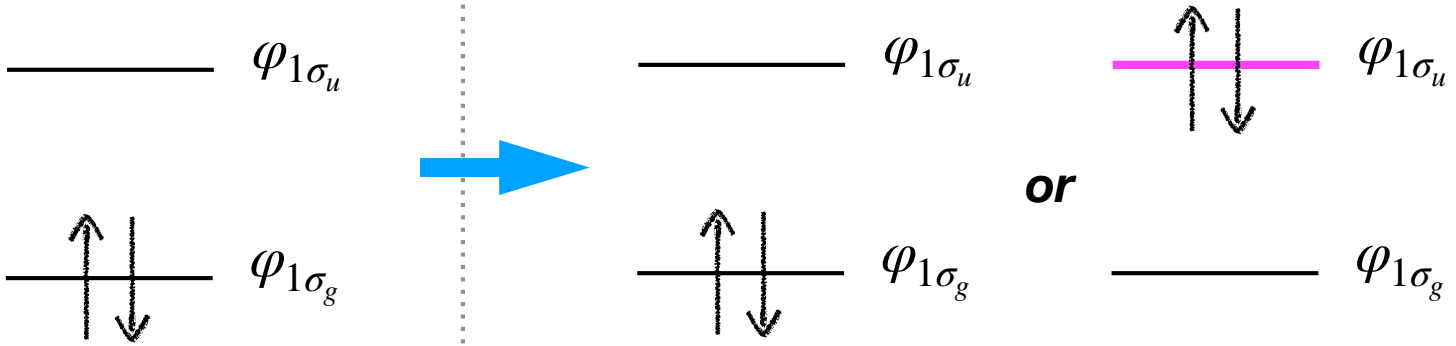
Multi-configurational wave function



minus *combination*

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

Multi-configurational wave function

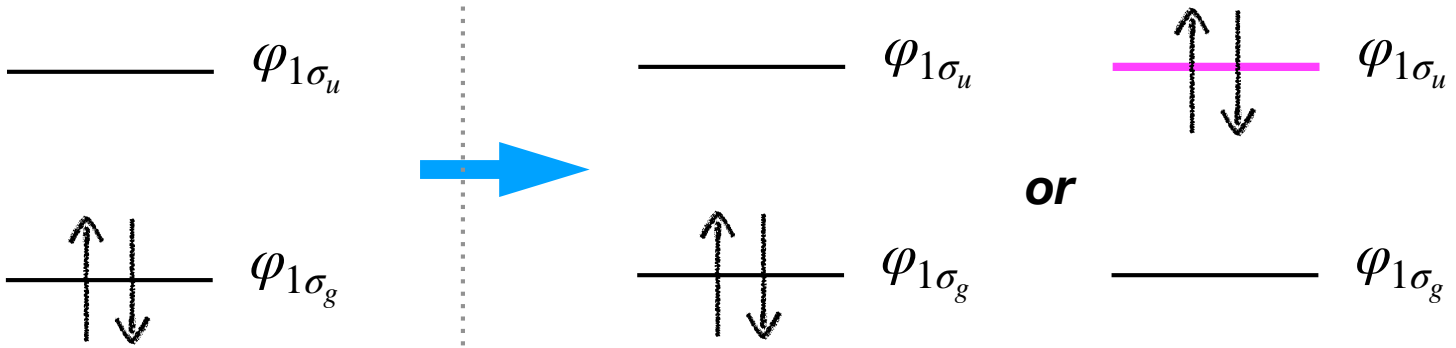


$$\varphi_{1\sigma_u}(\mathbf{r}) = \frac{1}{\sqrt{2}}\left(\chi_{s_A}(\mathbf{r}) - \chi_{s_B}(\mathbf{r})\right)$$

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

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

Multi-configurational wave function

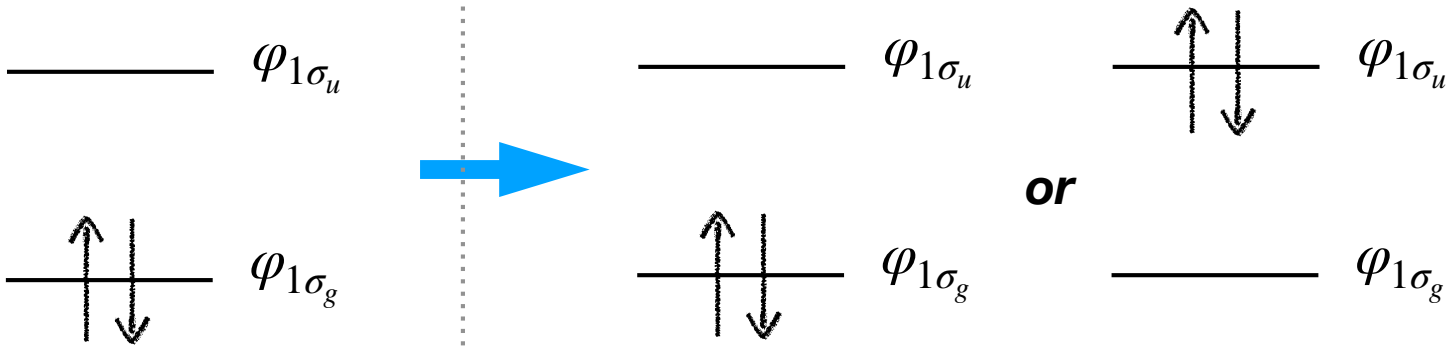


$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

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

H ..... H H ..... H

Multi-configurational wave function



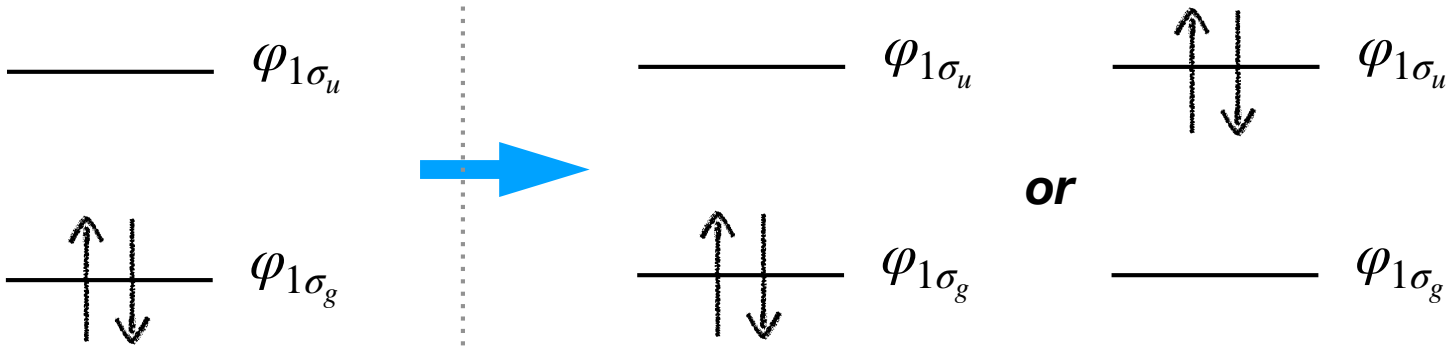
$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

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



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

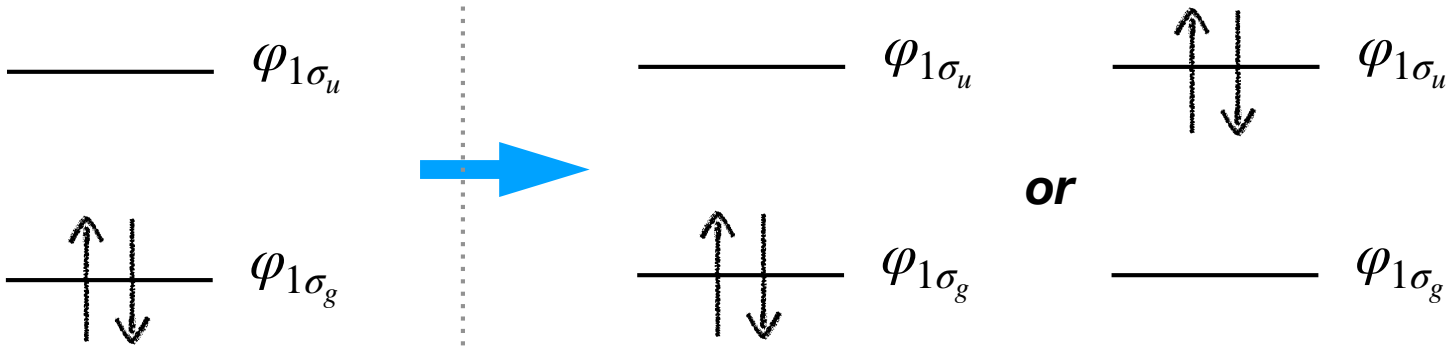
Localised picture →

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

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

Strong electron correlation

Multi-configurational wave function



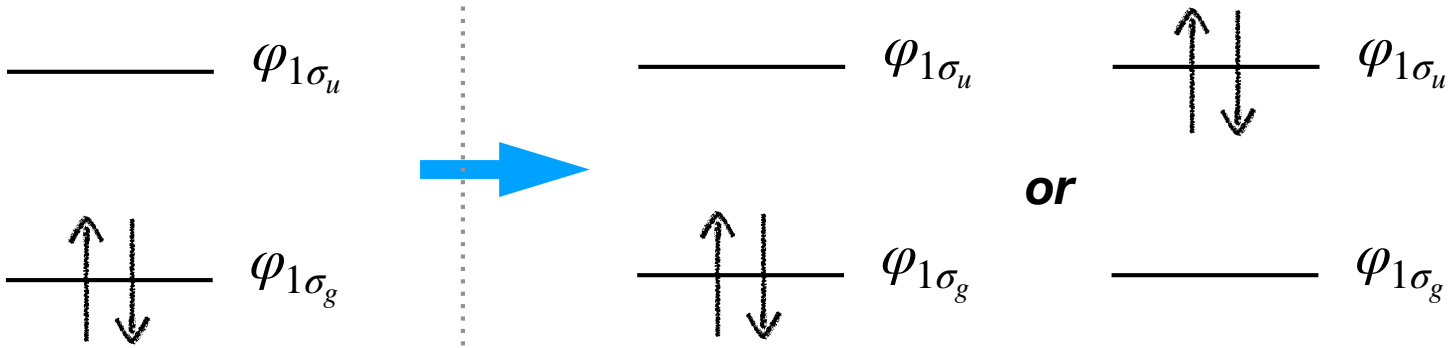
Delocalised *picture*

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

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

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

Multi-configurational wave function



Delocalised *picture*

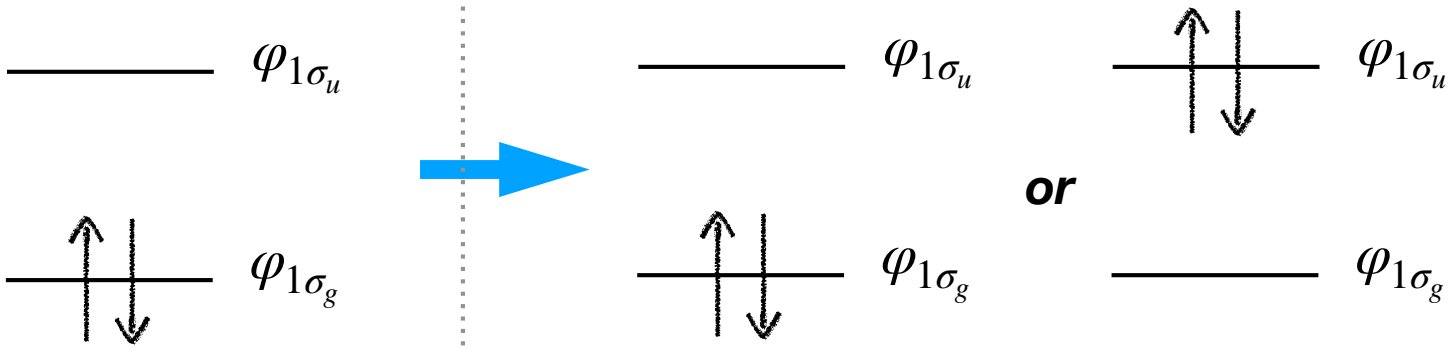
$$\equiv \frac{1}{\sqrt{2}}\left(\varphi_{1\sigma_g}(\mathbf{r}_1)\varphi_{1\sigma_g}(\mathbf{r}_2) - \varphi_{1\sigma_u}(\mathbf{r}_1)\varphi_{1\sigma_u}(\mathbf{r}_2)\right)$$

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**

Multi-configurational wave function



Delocalised *picture*

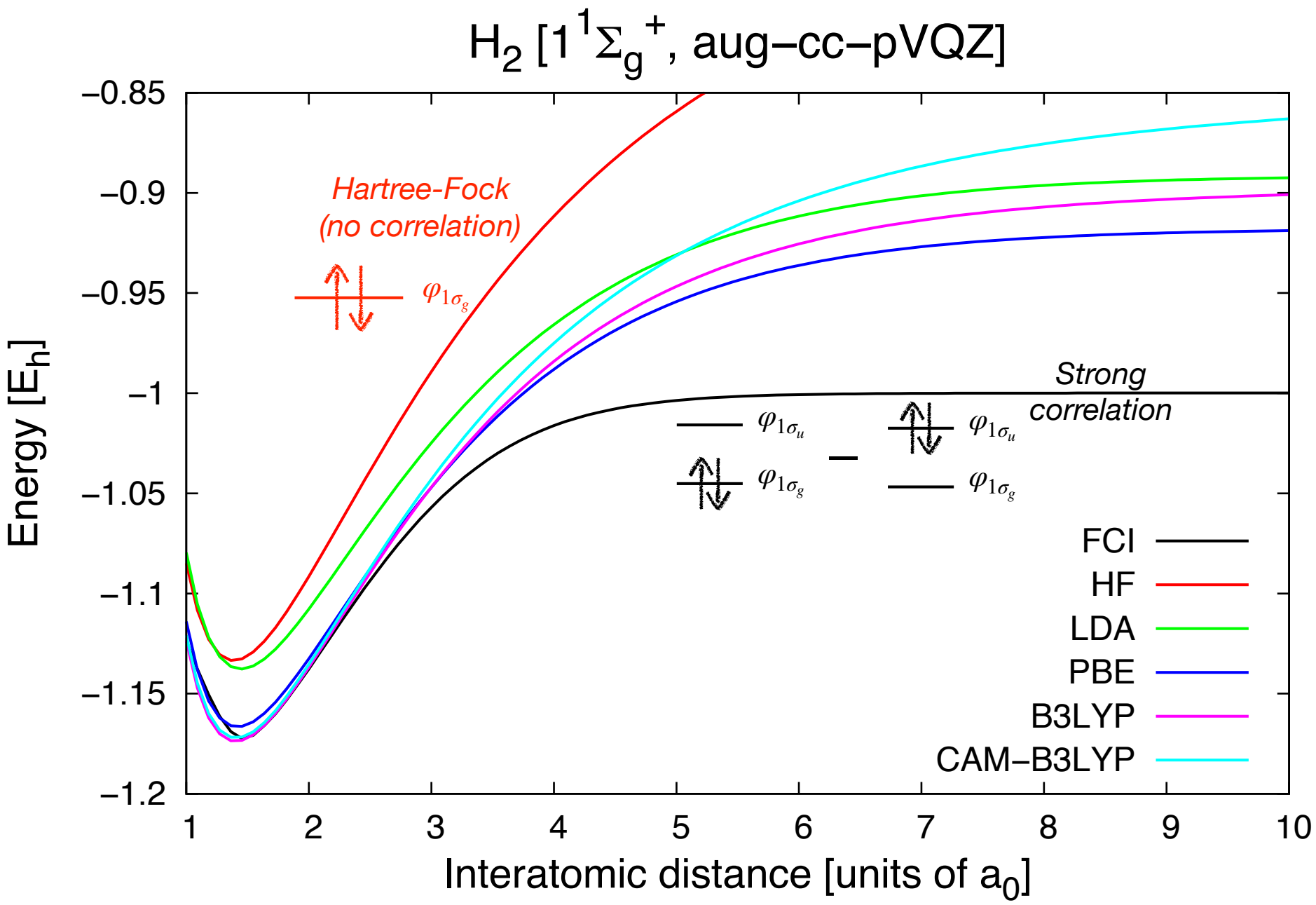
Strong multi-configurational
character of the electronic structure

correlation effect

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

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

H ..... H H ..... H


H2 [1 1Σg+, aug–cc–pVQZ]
Energy [Eh]
Interatomic distance [units of a0]
–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)
φ1σg
Strong
correlation
φ1σu
φ1σg
–
φ1σu
φ1σg
FCI
HF
LDA
PBE
B3LYP
CAM–B3LYP