An introduction to density-functional theory

Emmanuel Fromager

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

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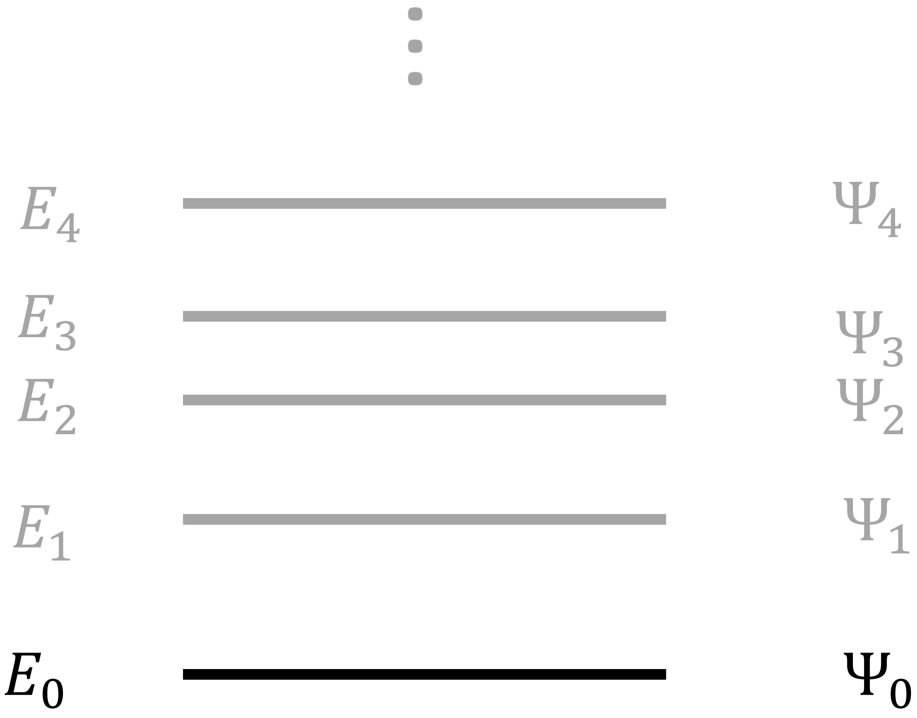
General principles of quantum mechanics

for the electronic structure problem

Schrödinger equation for the *ground* state



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

N-electron Schrödinger equation for the *ground* state

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

where $\Psi_0 \equiv \Psi_0(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$, $\mathbf{x}_i \equiv (\mathbf{r}_i, \sigma_i) \equiv (x_i, y_i, z_i, \sigma_i = \pm\frac{1}{2})$ for $i = 1, 2, \ldots, N$,

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

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

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

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

Rayleigh-Ritz variational principle

$$E_0 \leq \underbrace{\frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}}_{\textbf{Expectation value of the energy}}$$

See Appendix A
for the proof

for the (arbitrary) trial N-electron wave function Ψ

Rayleigh-Ritz variational principle

$$E_0 \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Quantum operator

$$\downarrow$$

$$\langle \Psi | \hat{\mathcal{O}} | \Psi \rangle \equiv \langle \Psi | \hat{\mathcal{O}} \Psi \rangle$$

$$= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \; \Psi^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \times \hat{\mathcal{O}} \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

Rayleigh-Ritz variational principle

$$E_0 \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

$$\langle \Psi | \Psi \rangle = 1$$

Usual normalisation condition

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

(Fictitious) non-interacting electrons

- Solving the Schrödinger equation for non-interacting electrons is *easy*.
- You “just" have to solve the Schrödinger equation for a *single electron*.

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

Proof: a *simple solution* to the N-electron non-interacting Schrödinger equation is

$$\Phi_0\equiv\varphi_1(\mathbf{x}_1)\times\varphi_2(\mathbf{x}_2)\times\ldots\times\varphi_N(\mathbf{x}_N)=\prod_{j=1}^{N}\varphi_j(\mathbf{x}_j) \qquad \leftarrow \textit{Hartree product!}$$

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

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- Solving the Schrödinger equation for non-interacting electrons is *easy*.
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Proof: a *simple solution* to the N-electron non-interacting Schrödinger equation is

spin-orbitals (one-electron wave functions)

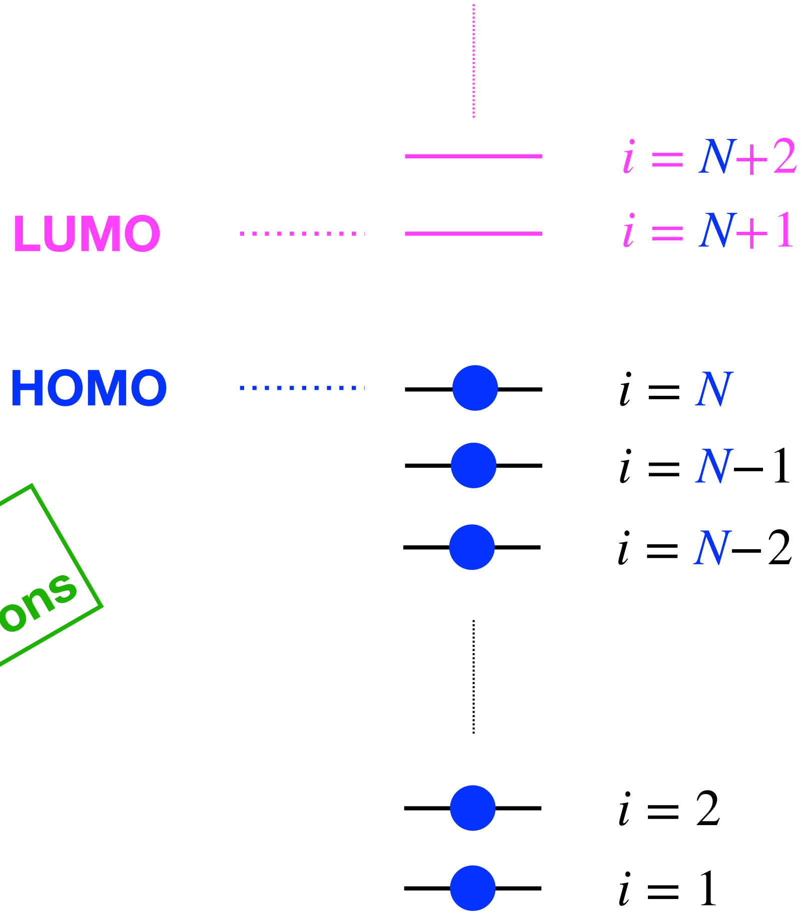
$$\Phi_0\equiv\varphi_1(\mathbf{x}_1)\times\varphi_2(\mathbf{x}_2)\times\ldots\times\varphi_N(\mathbf{x}_N)=\prod_{j=1}^{N}\varphi_j(\mathbf{x}_j) \qquad \leftarrow \textit{Hartree product!}$$

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

Total *noninteracting*
N-electron ***energy***

The one-electron picture

$$\left[-\frac{\nabla_{\mathbf{r}}^2}{2}+v(\mathbf{r})\right]\varphi_i(\mathbf{x})=\varepsilon_i\varphi_i(\mathbf{x})$$



$i = N+2$

LUMO $i = N+1$

HOMO $i = N$

$i = N-1$

$i = N-2$

$i = 2$

$i = 1$

Exact for noninteracting electrons

(Real) interacting many-electron problem

- Before addressing the true (interacting) problem we should keep in mind that electrons are *fermions*.
- Consequently, they should be described by *Slater determinants* instead of Hartree products.
- Therefore, in the particular case of *two electrons*, we have

$$\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) \quad \longrightarrow \quad \Phi_0 \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \overset{\textit{Antisymmetric}}{\underbrace{\Big[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1)\Big]}_{= 0 \text{ if } \mathbf{x}_1 = \mathbf{x}_2}}.$$

Hartree-Fock (HF) approximation

$$E_0^{\mathrm{HF}} = \min_{\underbrace{\Phi \equiv |\varphi_1 \varphi_2 \ldots \varphi_N|}_{\textbf{Slater determinant}}} \langle \Phi | \hat{H} | \Phi \rangle$$

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi | \hat{W}_{\mathrm{ee}} | \Phi \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|} + \ldots$$

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi | \hat{W}_{\mathrm{ee}} | \Phi \rangle = \underbrace{\frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|}} + \ldots$$

$$\shortparallel$$

Electron density (local)

$$\frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_{\Phi}(\mathbf{r}) n_{\Phi}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Hartree (or Coulomb) energy

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi | \hat{W}_{\mathrm{ee}} | \Phi \rangle = \frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2\right)\left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2\right)}{|\mathbf{r}-\mathbf{r}'|}$$

$$-\frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} \varphi_i^*(\mathbf{x})\varphi_i(\mathbf{x}')\right)\left(\sum_{j=1}^{N} \varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}')\right)}{|\mathbf{r}-\mathbf{r}'|}$$

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi | \hat{W}_{\text{ee}} | \Phi \rangle = \frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} |\varphi_i(\mathbf{x})|^2 \right) \left(\sum_{j=1}^{N} |\varphi_j(\mathbf{x}')|^2 \right)}{|\mathbf{r} - \mathbf{r}'|}$$

$$-\frac{1}{2} \int d\mathbf{x} \int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N} \varphi_i^*(\mathbf{x}) \varphi_i(\mathbf{x}') \right) \left(\sum_{j=1}^{N} \varphi_j(\mathbf{x}) \varphi_j^*(\mathbf{x}') \right)}{|\mathbf{r} - \mathbf{r}'|}$$

Exchange energy

Two-electron repulsion energy of an N-electron Slater determinant

$$\langle \Phi | \hat{W}_{\text{ee}} | \Phi \rangle = \frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}' \frac{\left(\sum_{i=1}^{N}|\varphi_i(\mathbf{x})|^2\right)\left(\sum_{j=1}^{N}|\varphi_j(\mathbf{x}')|^2\right)}{|\mathbf{r}-\mathbf{r}'|}$$

$$-\frac{1}{2}\int d\mathbf{x}\int d\mathbf{x}'\frac{\boxed{\left(\sum_{i=1}^{N} \varphi_i^*(\mathbf{x})\varphi_i(\mathbf{x}')\right)}\boxed{\left(\sum_{j=1}^{N} \varphi_j(\mathbf{x})\varphi_j^*(\mathbf{x}')\right)}}{|\mathbf{r}-\mathbf{r}'|}$$

One-electron reduced density matrix (nonlocal)

(Real) interacting many-electron problem

- Before addressing the true (interacting) problem we should keep in mind that electrons are *fermions*.

- Consequently, they should be described by *Slater determinants* instead of Hartree products.

- Therefore, in the particular case of *two electrons*, we have

$$\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) \quad \longrightarrow \quad \Phi_0 \equiv \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_1(\mathbf{x}_2) \\ \varphi_2(\mathbf{x}_1) & \varphi_2(\mathbf{x}_2) \end{vmatrix} = \frac{1}{\sqrt{2}} \Big[\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2) - \varphi_1(\mathbf{x}_2)\varphi_2(\mathbf{x}_1)\Big].$$

……

- When computing the two-electron repulsion energy $\left\langle \Phi_0 \middle| \hat{W}_{\rm ee} \middle| \Phi_0 \right\rangle$ we describe the so-called *Hartree* (i.e. electrostatic) and *exchange* energies.

- Finally, Φ_0 *cannot* be the exact solution to the interacting Schrödinger equation [whatever choice is made for the spin-orbitals $\{\varphi_i(\mathbf{x})\}_{i=1,2,\ldots}$]. **See Appendix B**

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

Key idea of regular (Kohn-Sham) density-functional theory

before we discuss technicalities

Mapping the interacting problem onto a non-interacting one

- Is it possible to *extract* the exact (interacting) ground-state energy E_0 *from a non-interacting system*?

- If yes, then it would lead to a huge *simplification* of the problem.

- Nevertheless, the question sounds a bit weird since the two-electron repulsion is completely ignored in a non-interacting system.

- One way to establish a *connection* between interacting and non-interacting worlds is to use the *electron density* as basic variable (instead of the wavefunction).

- Electron density for a *non-interacting* system: $n_{\Phi_0}(\mathbf{r}) = \sum_{\sigma=\pm\frac{1}{2}} \sum_{i=1}^{N} |\varphi_i(\mathbf{r},\sigma)|^2$

- Electron density for an *interacting* system:

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

- The so-called *Kohn–Sham* non-interacting system (from which E_0 can be determined) is such that $\boxed{n_{\Phi_0}(\mathbf{r}) = n_{\Psi_0}(\mathbf{r})}$.

Exactification of the one-electron picture in density-functional theory

True Hamiltonian

$$\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$$

True density

↓

Bare noninteracting
Hamiltonian

$$\hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$$

True density?

Obviously no!

Exactification of the one-electron picture in density-functional theory

True Hamiltonian

$$\hat{T}+\hat{W}_{\rm ee}+\sum_{i=1}^{N}v(\mathbf{r}_i)\times$$

True density

$$\Big\downarrow$$

Kohn-Sham* *Hamiltonian

$$\hat{T}+\sum_{i=1}^{N}\underbrace{\Big(v(\mathbf{r}_i)+v_{\rm Hxc}(\mathbf{r}_i)\Big)}_{\text{Kohn-Sham potential}}\times$$

True density?

Yes!

Exactification of the one-electron picture in density-functional theory

True Hamiltonian

$$\hat{T} + \hat{W}_{\mathrm{ee}} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$$

True density

Kohn-Sham ***Hamiltonian***

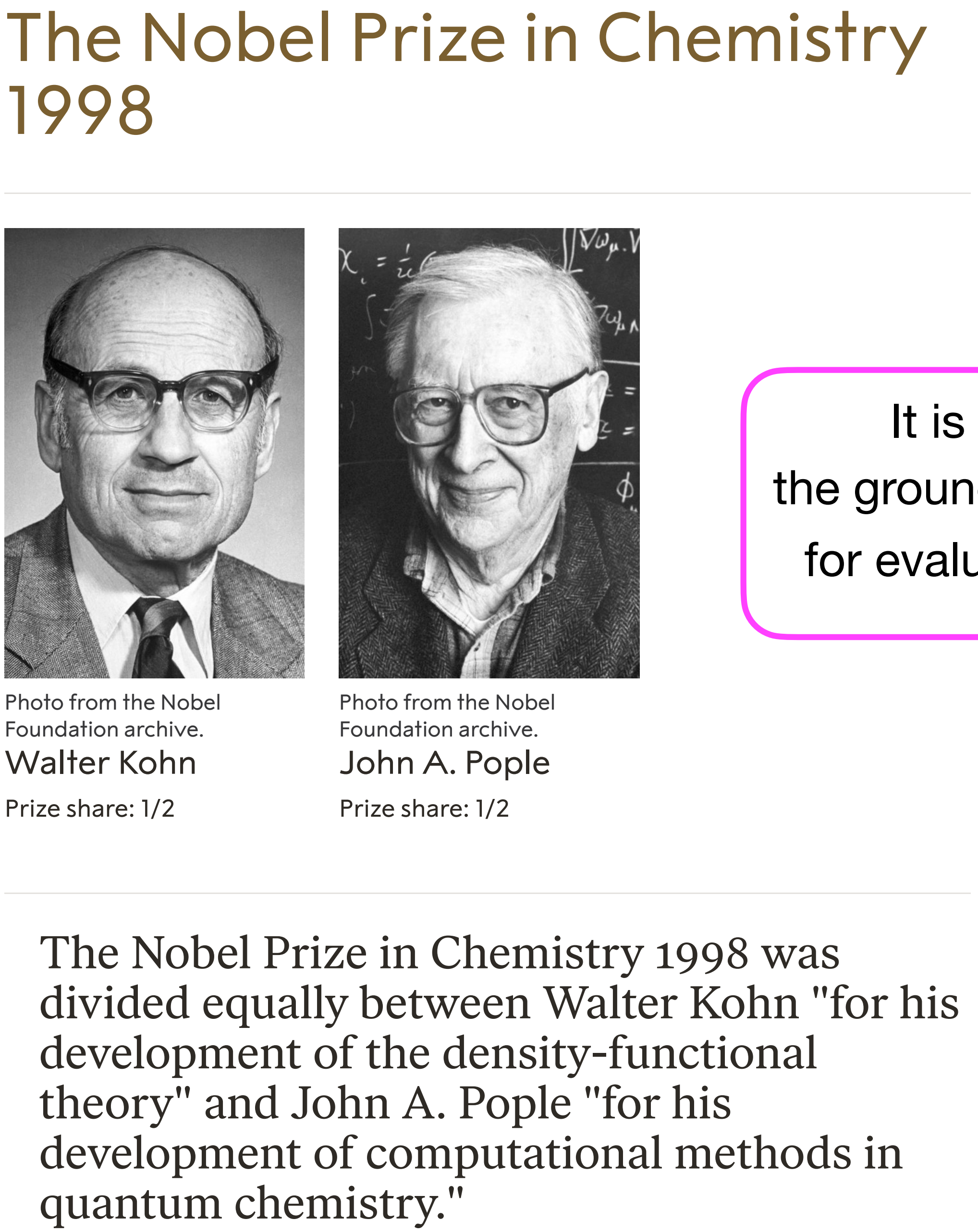
$$\hat{T} + \sum_{i=1}^{N} \left(v(\mathbf{r}_i) + \underbrace{\overset{???}{v_{\mathrm{Hxc}}(\mathbf{r}_i)}} \right) \times$$

True density?

Yes!

(A priori unknown) Hartree-exchange-correlation (Hxc)
local potential

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.

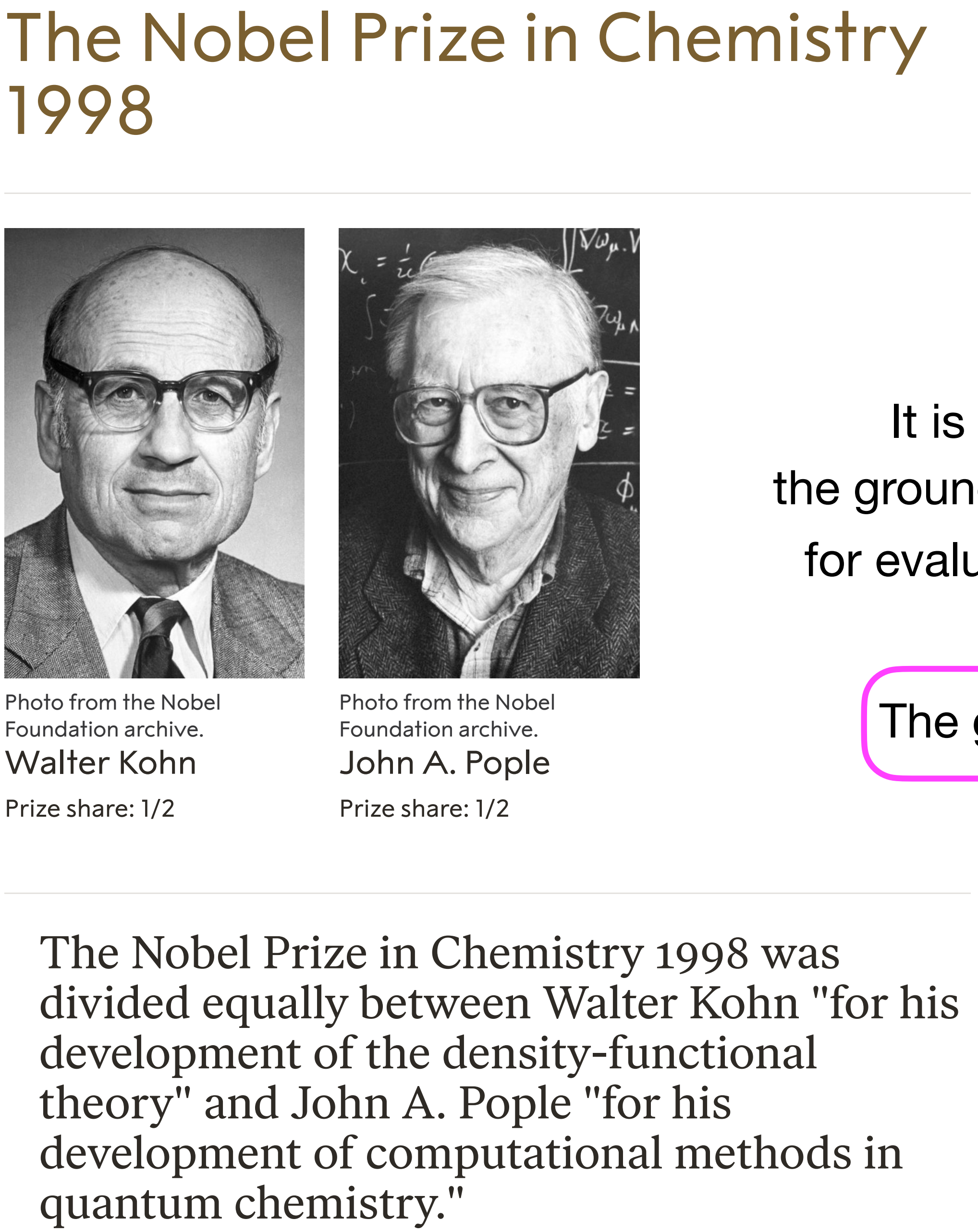
John A. Pople

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.***

Interlude on the electron density

and its evaluation from the total energy

An important observation to make before we continue...

The *one-electron potential energy* is an *explicit functional of the density*:

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

See Appendix C
for the proof

Potential-density relation

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

Potential-density relation

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

$$E_0 \equiv E_0[v] = \min_{\Psi} \frac{\langle \Psi | \hat{H}[v] | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \langle \Psi_0[v] | \hat{H}[v] | \Psi_0[v] \rangle$$

Potential-density relation

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$$\boxed{v(\mathbf{r}) \rightarrow v(\mathbf{r}) + \delta v(\mathbf{r})}$$

$$\delta E_0[v] = \langle \Psi_0[v] | \delta \hat{H}[v] | \Psi_0[v] \rangle$$

Hellmann-Feynman theorem

Potential-density relation

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

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$$\boxed{v(\mathbf{r}) \rightarrow v(\mathbf{r}) + \delta v(\mathbf{r})}$$

Hellmann-Feynman theorem

$$\delta E_0[v] = \langle \Psi_0[v] | \delta \hat{H}[v] | \Psi_0[v] \rangle$$

$$= \left\langle \Psi_0[v] \middle| \sum_{i=1}^{N} \delta v(\mathbf{r}_i) \times \middle| \Psi_0[v] \right\rangle$$

Potential-density relation

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

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$$\boxed{v(\mathbf{r}) \rightarrow v(\mathbf{r}) + \delta v(\mathbf{r})}$$

Hellmann-Feynman theorem

$$\delta E_0[v] = \langle \Psi_0[v] | \delta\hat{H}[v] | \Psi_0[v] \rangle$$

$$= \left\langle \Psi_0[v] \middle| \sum_{i=1}^{N} \delta v(\mathbf{r}_i) \times \middle| \Psi_0[v] \right\rangle$$

$$= \int d\mathbf{r}\, \delta v(\mathbf{r})\, n_{\Psi_0[v]}(\mathbf{r})$$

Potential-density relation

$$\frac{\delta E_0[v]}{\delta v(\mathbf{r})} = n_{\Psi_0[v]}(\mathbf{r})$$

Potential-density relation

Interacting case

$$\boxed{\frac{\delta E_0[v]}{\delta v(\mathbf{r})} = n_{\Psi_0[v]}(\mathbf{r})}$$

Noninteracting case

$$\frac{\delta \mathscr{E}_0[v]}{\delta v(\mathbf{r})} = n_{\Phi_0[v]}(\mathbf{r})$$

Same potential-density relation in the noninteracting case

Ground-state ***energy*** *of* $\hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$

$$\frac{\delta \mathcal{E}_0[v]}{\delta v(\mathbf{r})} = n_{\Phi_0[v]}(\mathbf{r})$$

Ground-state ***wave function*** *of* $\hat{T} + \sum_{i=1}^{N} v(\mathbf{r}_i) \times$

Variational principle of DFT

Levy's constrained search formalism

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

Levy’s constrained search formalism

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

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

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

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

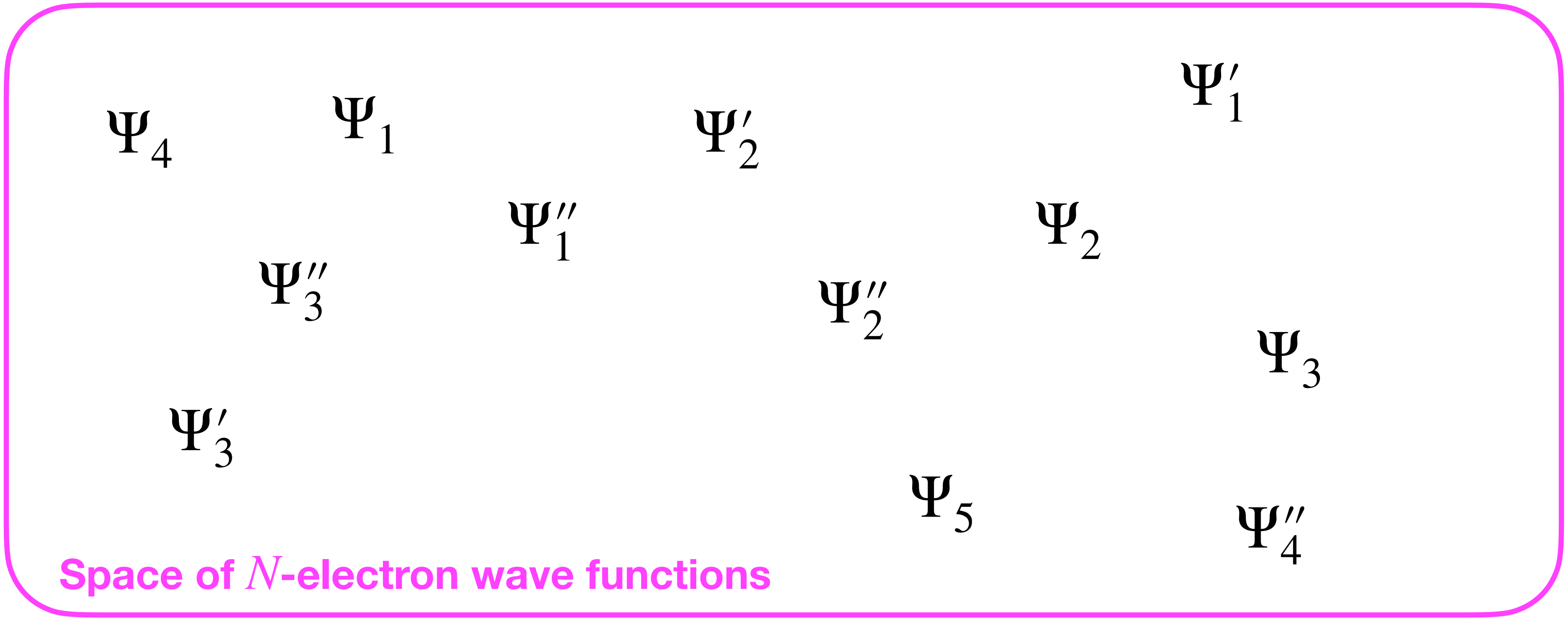
Minimisation over ***densities*** n

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

Levy's constrained search formalism

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

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



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Levy's constrained search formalism

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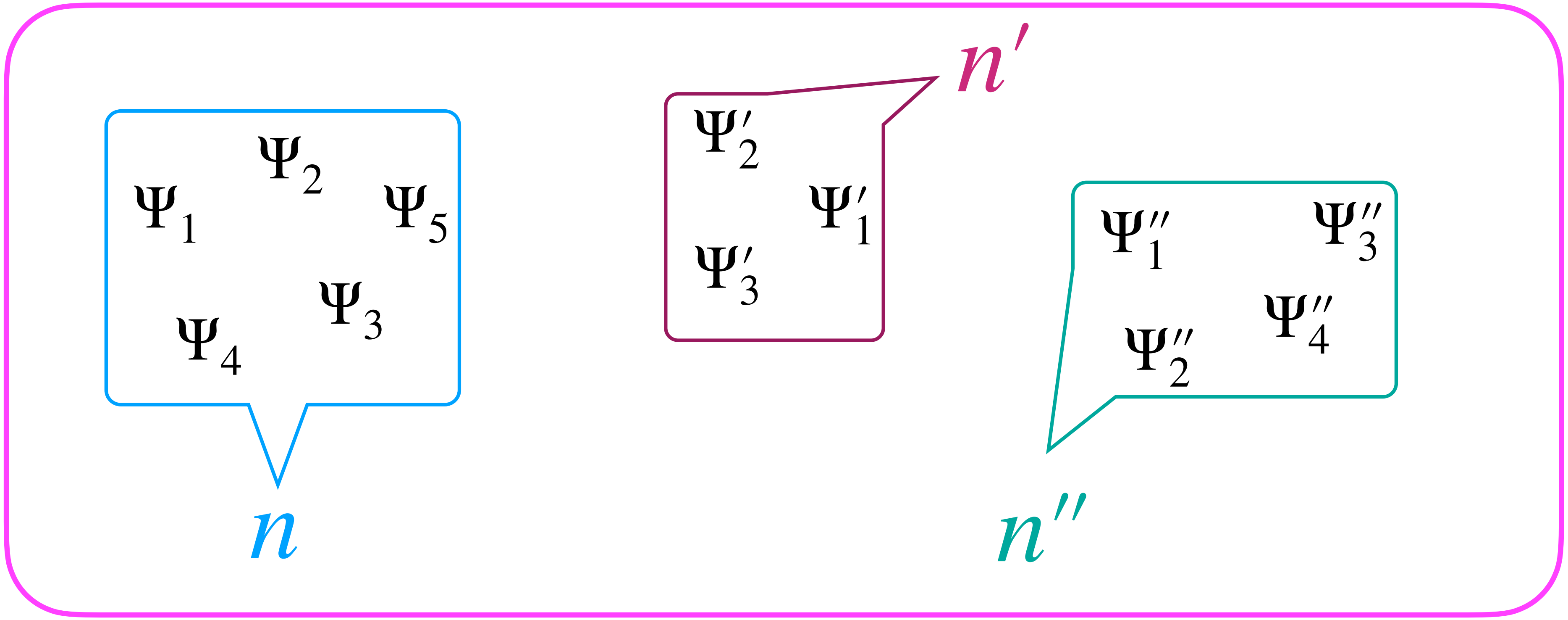
$$= \boxed{\min_{n} \left\{ \min_{\Psi \to n} \right.} \langle \Psi | \hat{H} | \Psi \rangle \left. \vphantom{\min_{\Psi \to n}} \right\}$$



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

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

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

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

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

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

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

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

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

Levy's constrained search formalism

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

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

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

Kohn-Sham DFT formalism

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

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

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(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).

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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*

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

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*

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

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

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

Holy grail of DFT!

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*

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

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, …).*

Let us find out what the exact density-functional KS potential is

and deduce the working equations of KS-DFT

Hohenberg-Kohn variational principles

Interacting case

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

Noninteracting case

$$\mathcal{E}_0[v] = \min_n \left\{ T_\mathrm{s}[n] + \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

Lieb maximization (for interacting electrons)

$$E_0[v] \leq F[n] + \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r})$$

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

Lieb maximization (for interacting electrons)

$$E_0[v] \leq F[n] + \boxed{\int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r})}$$

$$E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \leq F[n]$$

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

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$$E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \leq F[n]$$

$$F[n] = \max_{v} \left\{ E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

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

Lieb maximization (for interacting electrons)

See Appendix D
for the proof

Makes sense because the Rayleigh-Ritz variational principle implies the ***concavity*** *in v of $E_0[v]$!*

$$F[n] = \max_{v} \left\{ E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

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

Lieb maximization (for interacting electrons)

$$\frac{\delta}{\delta v(\mathbf{r})}\left\{E_0[v]-\int d\mathbf{r}\,v(\mathbf{r})\,n(\mathbf{r})\right\}\Bigg|_{\boxed{v=v[n]}}=0 \quad\Leftrightarrow\quad \underbrace{\frac{\delta E_0[v]}{\delta v(\mathbf{r})}\Bigg|_{v=v[n]}=n(\mathbf{r})}$$

Maximizing potential → *Ground-state density*

$$F[n]=\max_{v}\left\{E_0[v]-\int d\mathbf{r}\,v(\mathbf{r})\,n(\mathbf{r})\right\}$$

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

Lieb maximization (for interacting electrons)

$$\left.\frac{\delta E_0[v]}{\delta v(\mathbf{r})}\right|_{v=v[n]} = n(\mathbf{r})$$

Maximizing potential

$$F[n] = \max_{v} \left\{ E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

This is a (more mathematical) ***reinterpretation*** *of the original* ***Hohenberg-Kohn theorem**!**

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

Lieb maximization (for interacting electrons)

$$\boxed{\frac{\delta F[n]}{\delta n(\mathbf{r})} = -v[n](\mathbf{r})}$$

Maximising interacting potential

$$\uparrow$$

$$F[n] = \max_{v} \left\{ E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

Lieb maximization for both interacting and noninteracting electrons

$$\boxed{\frac{\delta F[n]}{\delta n(\mathbf{r})} = -v[n](\mathbf{r})}$$

Maximising interacting potential

$$F[n] = \max_{v} \left\{ E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

$$T_{\mathrm{s}}[n] = \max_{v} \left\{ \mathcal{E}_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

$$\boxed{\frac{\delta T_{\mathrm{s}}[n]}{\delta n(\mathbf{r})} = -v^{\mathrm{KS}}[n](\mathbf{r})}$$

Maximising *noninteracting* (KS) potential

Application to the system under study

with nuclear potential $v_{\mathrm{ne}}(\mathbf{r})$

Known

$$\left.\frac{\delta F[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v[n_0](\mathbf{r}) = -v_{\mathrm{ne}}(\mathbf{r})$$

Unknown

Application to the system under study

with nuclear potential $v_{\mathrm{ne}}(\mathbf{r})$

$$\left.\frac{\delta F[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v[n_0](\mathbf{r}) = -v_{\mathrm{ne}}(\mathbf{r})$$

$$\left.\frac{\delta T_{\mathrm{s}}[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v^{\mathrm{KS}}[n_0](\mathbf{r})$$

Our target

Application to the system under study

with nuclear potential $v_{\mathrm{ne}}(\mathbf{r})$

$$\left.\frac{\delta F[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v[n_0](\mathbf{r}) = -v_{\mathrm{ne}}(\mathbf{r})$$

$$\left.\frac{\delta T_{\mathrm{s}}[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v^{\mathrm{KS}}[n_0](\mathbf{r})$$

$$v^{\mathrm{KS}}[n_0](\mathbf{r}) = \frac{\delta}{\delta n(\mathbf{r})}\Big(- F[n] + F[n] - T_{\mathrm{s}}[n]\Big)\Big|_{n=n_0}$$

Application to the system under study

with nuclear potential $v_{\rm ne}(\mathbf{r})$

$$\left.\frac{\delta F[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v[n_0](\mathbf{r}) = -v_{\rm ne}(\mathbf{r})$$

$$\left.\frac{\delta T_{\rm s}[n]}{\delta n(\mathbf{r})}\right|_{n=n_0} = -v^{\rm KS}[n_0](\mathbf{r})$$

$$v^{\rm KS}[n_0](\mathbf{r}) = \left.\frac{\delta}{\delta n(\mathbf{r})}\Big(-F[n] + F[n] - T_{\rm s}[n]\Big)\right|_{n=n_0}$$

$$\boxed{v^{\rm KS}[n_0](\mathbf{r}) = v_{\rm ne}(\mathbf{r}) + \left.\frac{\delta E_{\rm Hxc}[n]}{\delta n(\mathbf{r})}\right|_{n=n_0}}$$

Self-consistent KS equations

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

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

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

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

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

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

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

Brief interlude on exact extensions of KS-DFT

Exact extensions of DFT from the Lieb maximization

Example 1: Hybrid DFT

$$F[n] = \max_{v} \left\{ E_0[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

Alternative to the usual KS decomposition

$$= F^{\mathrm{HF}}[n] + \overline{E}_{\mathrm{c}}[n]$$

$$F^{\mathrm{HF}}[n] = \max_{v} \left\{ E_0^{\mathrm{HF}}[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

Density-functional ***exactification*** *of the Hartree-Fock approximation*

(Rigorous foundation for the so-called ***hybrid functionals***)

Exact extensions of DFT from the Lieb maximization

Example 2: Ensemble DFT of charged electronic excitations

$$E_0[v] \equiv E_0^N[v] \quad \longrightarrow \quad \underbrace{E_0^{N,\xi}[v] = \left(1-2\xi\right) E_0^N[v] + \xi E_0^{N+1}[v] + \xi E_0^{N-1}[v]}_{\text{Ensemble energy}}$$

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
B. Senjean and E. Fromager, Int. J. Quantum Chem. 2020; 120:e26190
F. Cernatic, B. Senjean, V. Robert, and E. Fromager, Top Curr Chem (Z) ***380****, 4 (2022).*

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$$\frac{\partial E_0^{N,\xi}[v]}{\partial \xi} = \left(E_0^{N+1}[v] - E_0^{N}[v]\right) + \left(E_0^{N-1}[v] - E_0^{N}[v]\right)$$

B. Senjean and E. Fromager, Phys. Rev. A ***98****, 022513 (2018).*
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$$\frac{\partial E_0^{N,\xi}[v]}{\partial \xi} = \overbrace{\left(E_0^{N+1}[v] - E_0^{N}[v]\right)}^{\textit{Affinity}} + \overbrace{\left(E_0^{N-1}[v] - E_0^{N}[v]\right)}^{\textit{ionization}}$$

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↓

$$F[n] \longrightarrow F^{\xi}[n] = \max_{v}\left\{E_0^{N,\xi}[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r})\right\}$$

DFT of charged excitations!

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Ensemble energy

$$F[n] \longrightarrow F^{\xi}[n] = \max_{v} \left\{ E_0^{N,\xi}[v] - \int d\mathbf{r}\, v(\mathbf{r})\, n(\mathbf{r}) \right\}$$

Exact connection between KS and true fundamental gaps! ⟶

$$= T_{\rm s}^{\xi}[n] + E_{\rm Hxc}^{\xi}[n]$$

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Brief review of standard density-functional approximations

Standard density-functional approximations (DFAs)

Local and semi-local functionals

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

LDA *(uniform electron gas)*

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

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

Generalized gradient approximations (GGAs):

LYP, PBE, …

$$\vdots$$

*C. **L**ee, W. **Y**ang, and R. G. **P**arr. Phys. Rev. B, 57:785, (**1988).***

*J. P. **P**erdew, K. **B**urke, M. **E**rnzerhof, Phys. Rev. Lett., 77, 3865 (**1996**).*

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Hybrid functionals

Hartree-Fock-like
exchange energy *(evaluated with generalised KS orbitals)*

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

B3LYP

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

Standard density-functional approximations (DFAs)

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

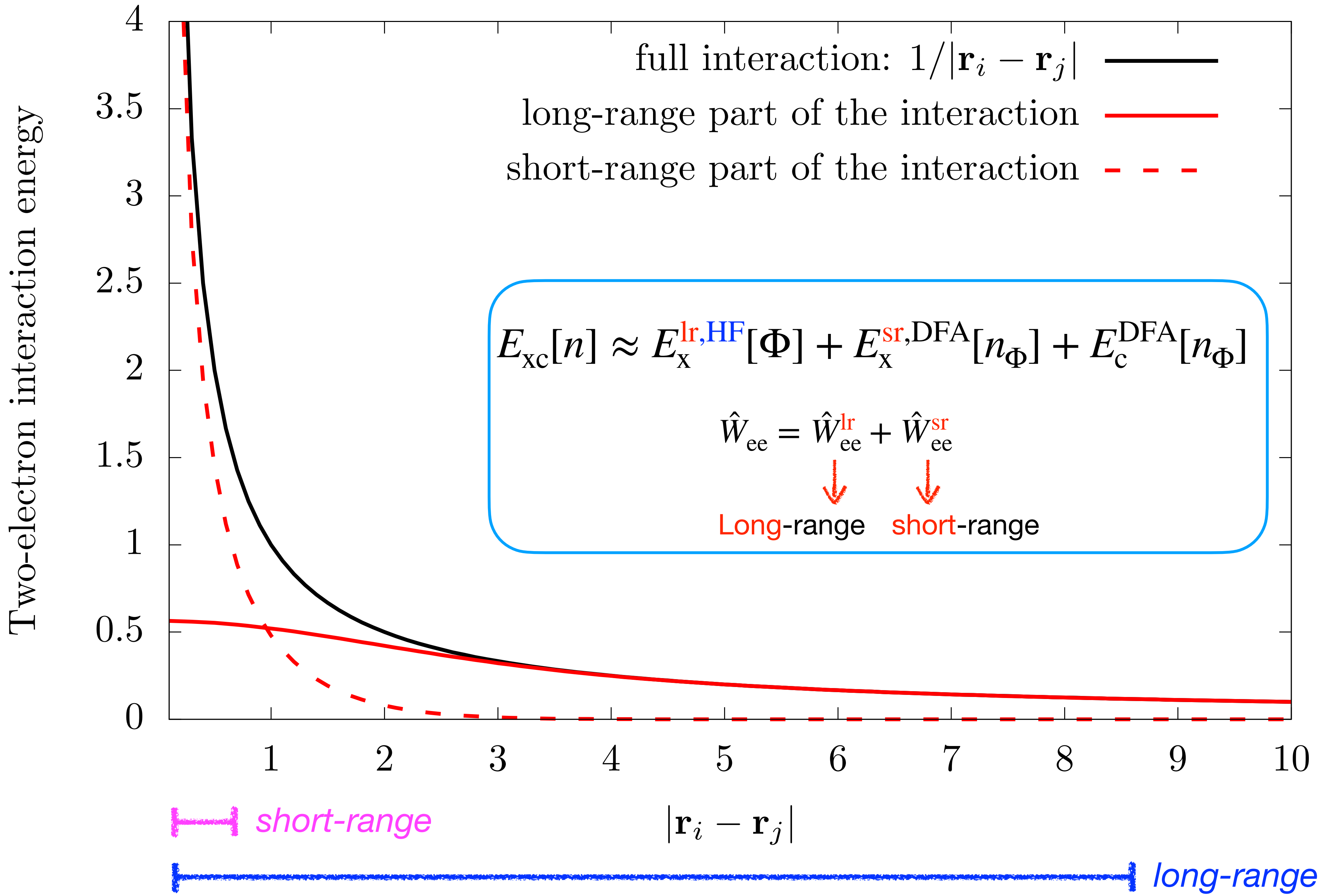
$$\vdots \qquad \hat{W}_{\mathrm{ee}} = \underset{\substack{\downarrow \\ \text{Long-range}}}{\hat{W}_{\mathrm{ee}}^{\mathrm{lr}}} + \underset{\substack{\downarrow \\ \text{short-range}}}{\hat{W}_{\mathrm{ee}}^{\mathrm{sr}}}$$

Range-separated hybrids

CAM-B3LYP

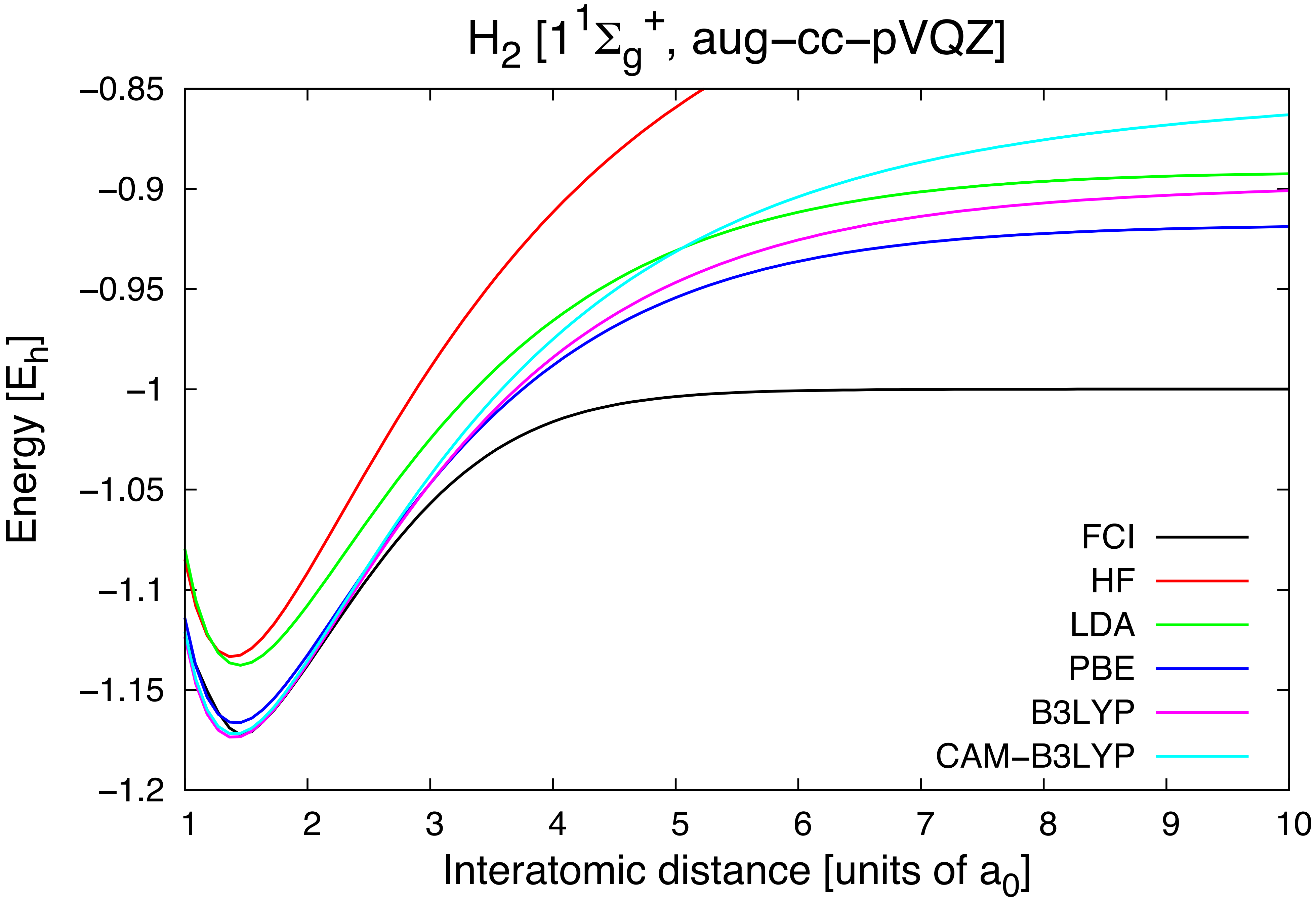
*Yanai, T.; Tew, D. P.; Handy, N. C., Chem. Phys. Lett., 393, 51-57 (**2004**).*

(arbitrary) range separation of the electronic repulsion

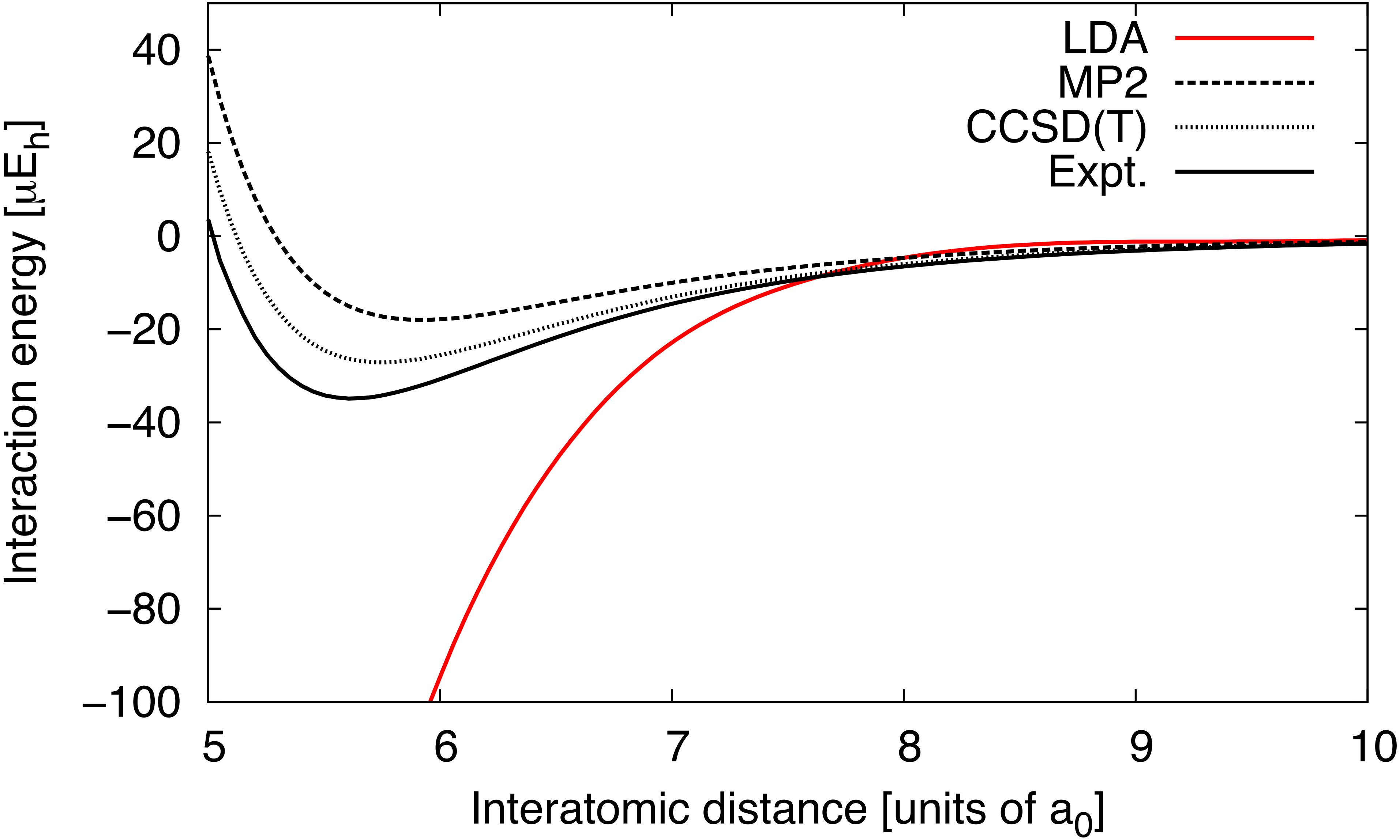


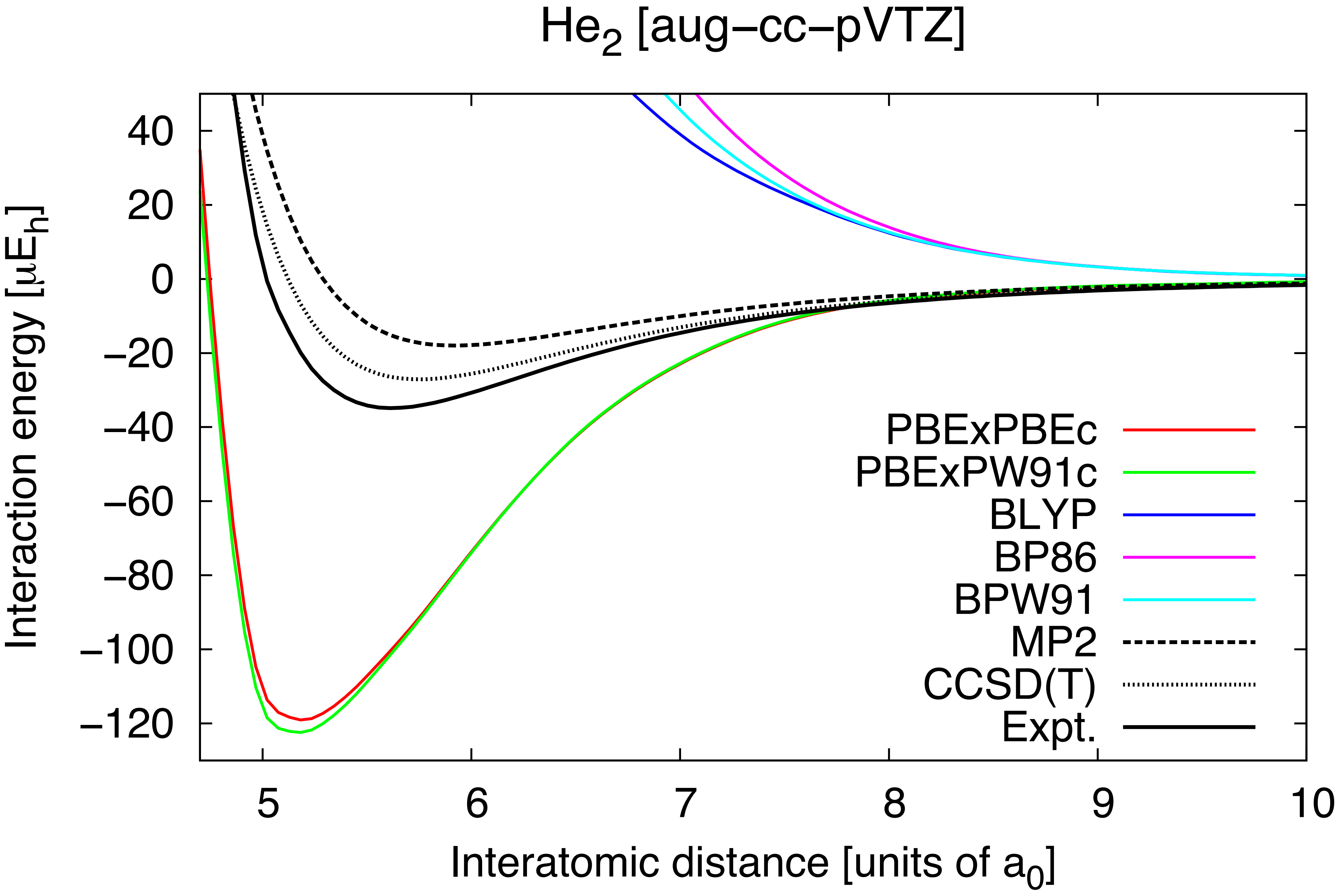
$$E_{\mathrm{xc}}[n] \approx E_{\mathrm{x}}^{\mathrm{lr,HF}}[\Phi] + E_{\mathrm{x}}^{\mathrm{sr,DFA}}[n_\Phi] + E_{\mathrm{c}}^{\mathrm{DFA}}[n_\Phi]$$

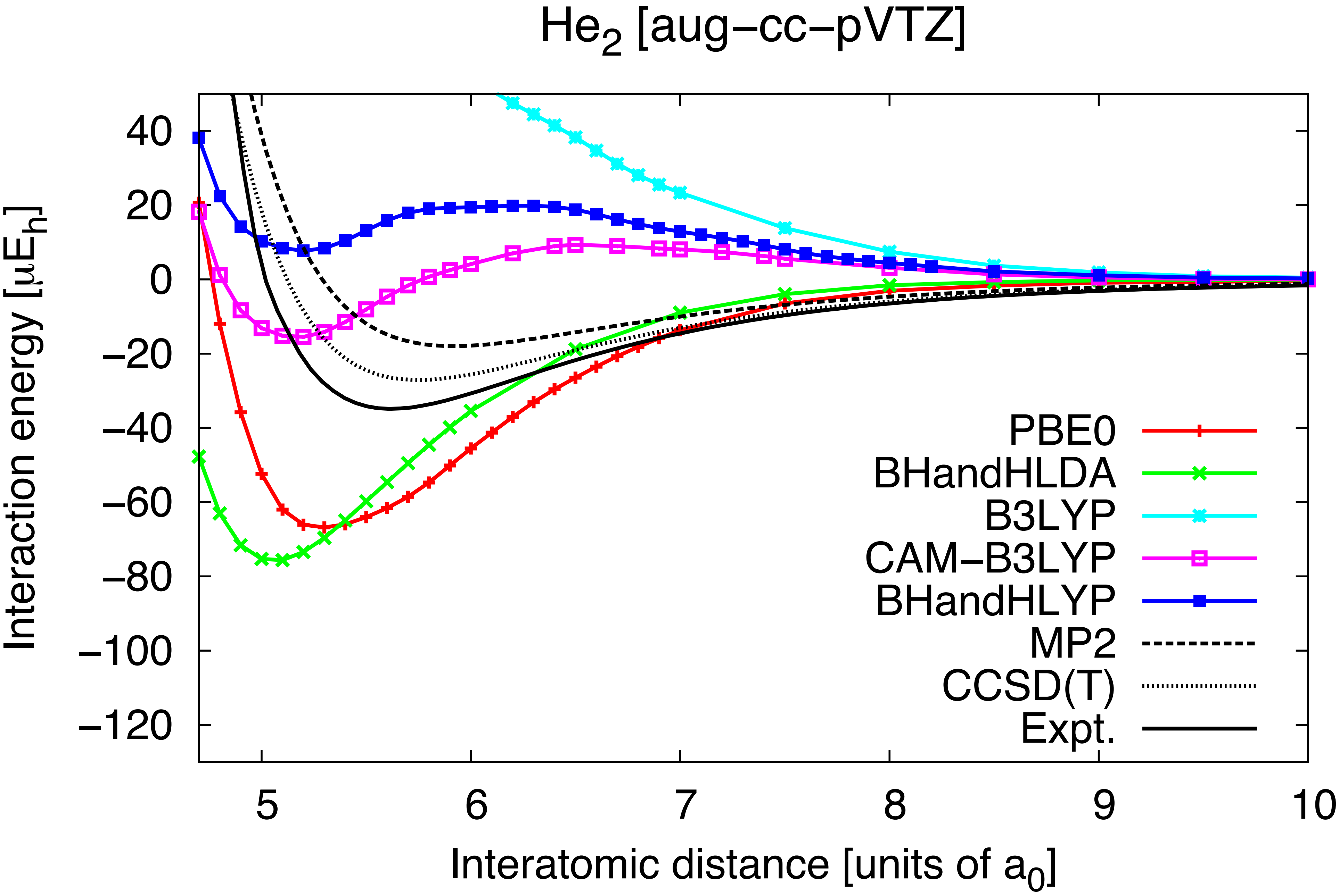
$$\hat{W}_{\mathrm{ee}} = \underset{\text{Long-range}}{\hat{W}_{\mathrm{ee}}^{\mathrm{lr}}} + \underset{\text{short-range}}{\hat{W}_{\mathrm{ee}}^{\mathrm{sr}}}$$


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
FCI
HF
LDA
PBE
B3LYP
CAM–B3LYP

He_2 [aug–cc–pVTZ]




He$_2$ [aug–cc–pVTZ]
Interaction energy [μE$_h$]
40
20
0
–20
–40
–60
–80
–100
–120
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
PBExPBEc
PBExPW91c
BLYP
BP86
BPW91
MP2
CCSD(T)
Expt.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Interaction energy [μE$_h$]
40
20
0
−20
−40
−60
−80
−100
−120
5
6
7
8
9
10
Interatomic distance [units of a$_0$]
PBE0
BHandHLDA
B3LYP
CAM–B3LYP
BHandHLYP
MP2
CCSD(T)
Expt.

PCCP

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DFT Exchange: Sharing Perspectives on the Workhorse of Quantum Chemistry and Materials Science [†]

Andrew M. Teale,[*AMT] Trygve Helgaker,[*TH] Andreas Savin,[*AS] Carlo Adamo,[CA] Bálint Aradi,[BA] Alexei V. Arbuznikov,[AVA] Paul W. Ayers,[PWA] Evert Jan Baerends,[EJB] Vincenzo Barone,[VB] Patrizia Calaminici,[PC] Eric Cancès,[EC] Emily A. Carter,[EAC] Pratim Kumar Chattaraj,[PKC] Henry Chermette,[HCh] Ilaria Ciofini,[IC] T. Daniel Crawford,[TDC] Frank De Proft,[FDP] John F. Dobson,[JD] Claudia Draxl,[CD] Thomas Frauenheim,[TF] Emmanuel Fromager,[EF] Patricio Fuentealba,[PF] Laura Gagliardi,[LG] Giulia Galli,[GG] Jiali Gao,[JG] Paul Geerlings,[PG] Nikitas Gidopoulos,[NG] Peter M. W. Gill,[PMWG] Paola Gori-Giorgi,[PGG] Andreas Görling,[AG] Tim Gould,[TG] Stefan Grimme,[SG] Oleg Gritsenko,[OG] Hans Jørgen Aagaard Jensen,[HJAaJ] Erin R. Johnson,[ERJ] Robert O. Jones,[ROJ] Martin Kaupp,[MK] Andreas M. Köster,[AK] Leeor Kronik,[LK] Anna I. Krylov,[AIK] Simen Kvaal,[SK] Andre Laestadius,[AL] Mel Levy,[MLe] Mathieu Lewin,[ML] Shubin Liu,[SL] Pierre-François Loos,[PFL] Neepa T. Maitra,[NM] Frank Neese,[FN] John P. Perdew,[JPP] Katarzyna Pernal,[KP] Pascal Pernot,[PPe] Piotr Piecuch,[PPi] Elisa Rebolini,[ER] Lucia Reining,[LR] Pina Romaniello,[PR] Adrienn Ruzsinszky,[AR] Dennis R. Salahub,[DRS] Matthias Scheffler,[MS] Peter Schwerdtfeger,[PSc] Viktor N. Staroverov,[VNS] Jianwei Sun,[JS] Erik Tellgren,[ET] David J. Tozer,[DJT] Samuel B. Trickey,[SBT] Carsten A. Ullrich,[CAU] Alberto Vela,[AV] Giovanni Vignale,[GV] Tomasz A. Wesolowski,[TW] Xin Xu[XX] Weitao Yang,[WY]

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In this paper, the history, present status, and future of density-functional theory (DFT) is informally reviewed and discussed by 70 workers in the field, including molecular scientists, materials scientists, method developers and practitioners. The format of the paper is that of a roundtable discussion, in which the participants express and exchange views on DFT in the form of 302 individual contributions, formulated as responses to a preset list of 26 questions. Supported by a bibliography of 777 entries, the paper represents a broad snapshot of DFT, anno 2022.

Appendices

Appendix A

Rayleigh–Ritz variational principle

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

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

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

where $|\Psi\rangle$ has been expanded in the orthonormal basis of the eigenvectors of $\hat{H}$, *i.e.*, $\hat{H}|\Psi_I\rangle \underset{I\geq 0}{=} E_I|\Psi_I\rangle$.

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

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

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

Appendix B

The true interacting many-electron problem

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

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

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

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

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

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

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

Proof of the nuclear potential energy simplification:

Appendix C

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

Electrons are indistinguishable particles

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

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

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

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

Change of variables in the integrals

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

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

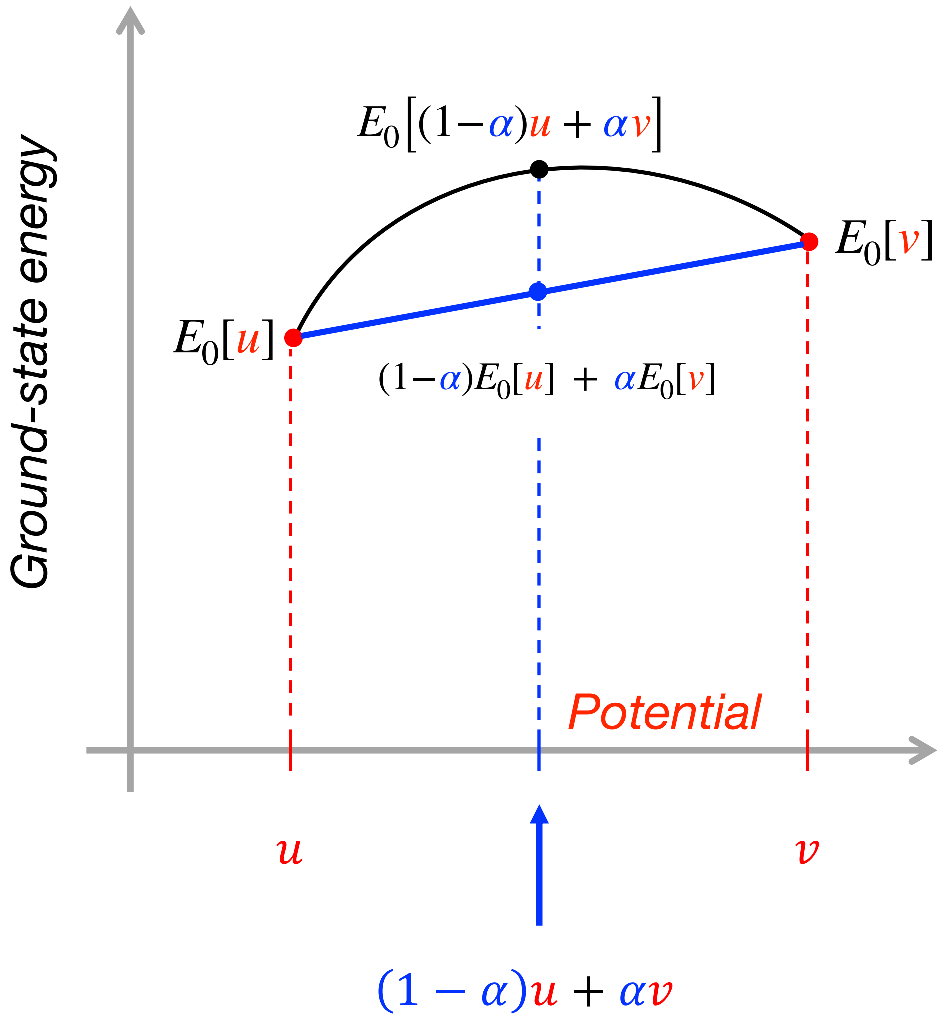
$$= N \int d\mathbf{x}_1 \ldots \int d\mathbf{x}_N \; v(\mathbf{r}_1) \times \left| \Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \right|^2$$

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

$$= \int d\mathbf{r}_1 \; v(\mathbf{r}_1) \times n_{\Psi}(\mathbf{r}_1)$$

Appendix D

Concavity in potential



$0 \leq \alpha \leq 1$

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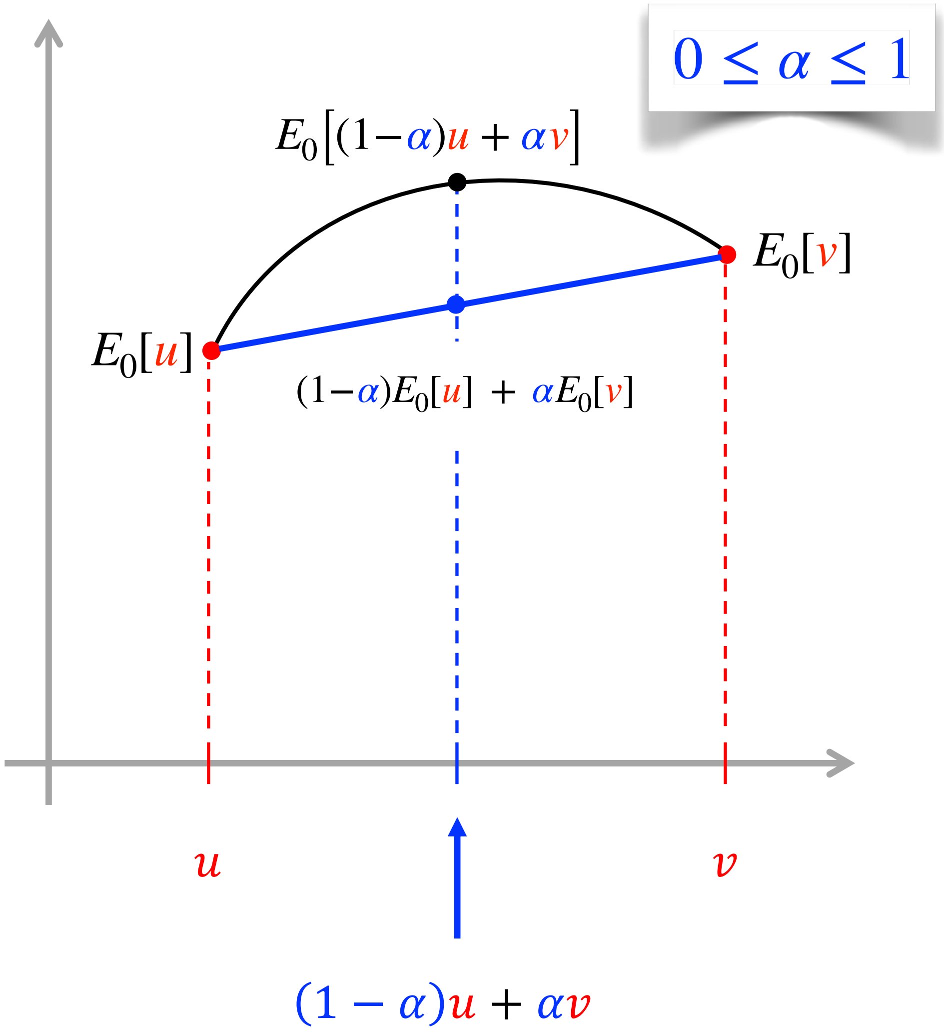
Appendix D

Concavity in potential

$$\langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + (1-\alpha)\hat{u} + \alpha\hat{v} | \Psi \rangle$$



$0 \leq \alpha \leq 1$

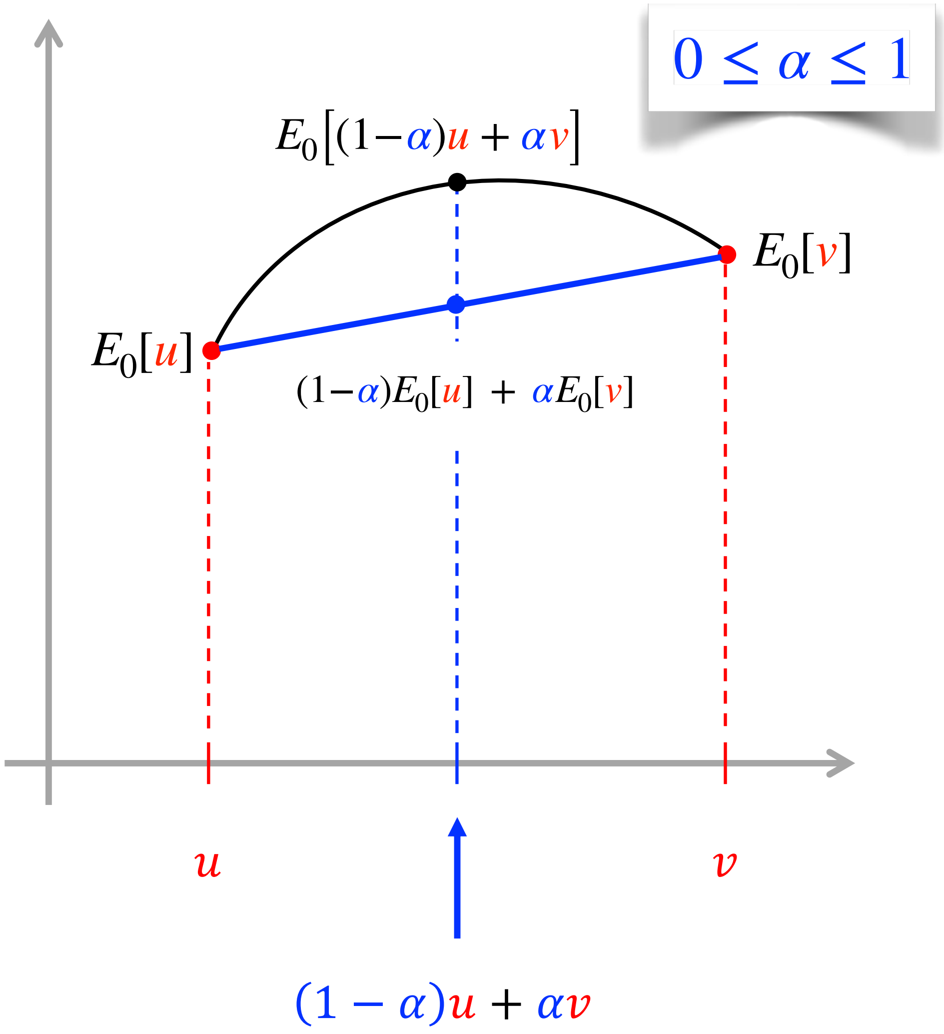
Appendix D

Concavity in potential

$$\hat{v} \equiv \sum_{i=1}^{N} v(\mathbf{r}_i) \times$$

$$\langle \Psi | \hat{T} + \hat{W}_{\rm ee} + (1-\alpha)\hat{u} + \alpha\hat{v} | \Psi \rangle$$

$$\hat{u} \equiv \sum_{i=1}^{N} u(\mathbf{r}_i) \times$$



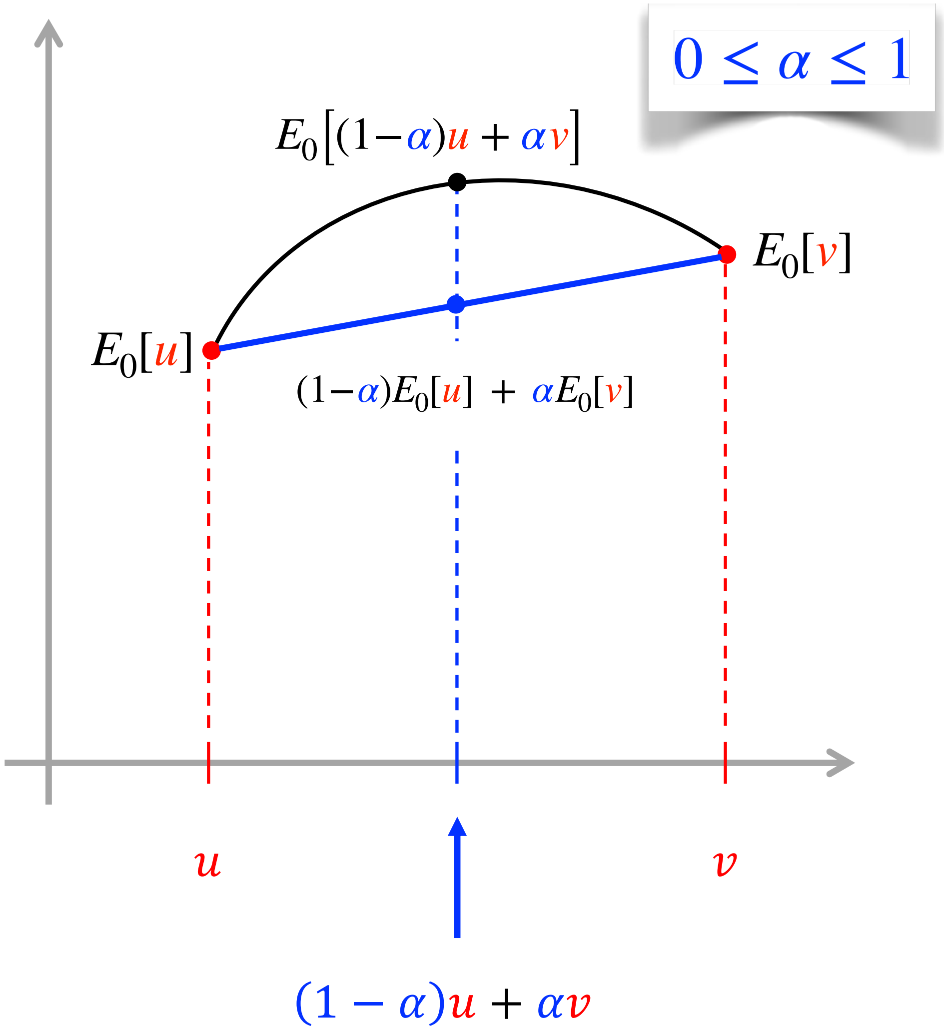
Appendix D

Concavity in potential

$$\langle\Psi|\hat{T}+\hat{W}_{\mathrm{ee}}+(1-\alpha)\hat{u}+\alpha\hat{v}|\Psi\rangle$$

$$=(1-\alpha)\langle\Psi|\hat{T}+\hat{W}_{\mathrm{ee}}+\hat{u}|\Psi\rangle$$

$$+\,\alpha\langle\Psi|\hat{T}+\hat{W}_{\mathrm{ee}}+\hat{v}|\Psi\rangle$$



$$0\le\alpha\le1$$

Appendix D

Concavity in potential

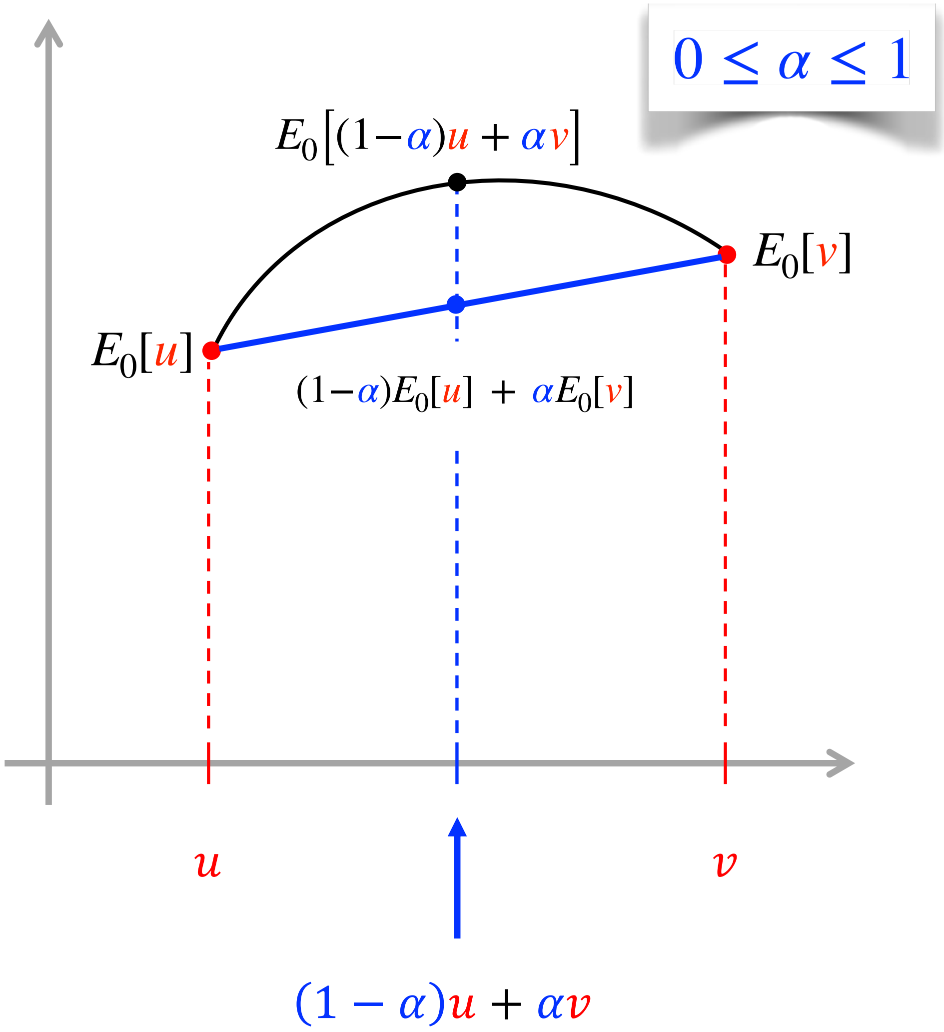
Rayleigh-Ritz variational principle

$$\langle\Psi|\hat{T}+\hat{W}_{\mathrm{ee}}+(1-\alpha)\hat{u}+\alpha\hat{v}|\Psi\rangle$$

$$=(1-\alpha)\boxed{\langle\Psi|\hat{T}+\hat{W}_{\mathrm{ee}}+\hat{u}|\Psi\rangle}\geq E_0[u]$$

$$+\,\alpha\boxed{\langle\Psi|\hat{T}+\hat{W}_{\mathrm{ee}}+\hat{v}|\Psi\rangle}\geq E_0[v]$$

$$\geq(1-\alpha)E_0[u]+\alpha E_0[v]$$



Appendix D

Concavity in potential

$$\langle \Psi | \hat{T} + \hat{W}_{\mathrm{ee}} + (1-\alpha)\hat{u} + \alpha\hat{v} | \Psi \rangle$$

$$\geq \; (1-\alpha)E_0[u] \; + \; \alpha E_0[v]$$

$$\Big\downarrow \min_{\Psi}$$

$$\boxed{E_0\big[(1-\alpha)u + \alpha v\big] \geq \; (1-\alpha)E_0[u] \; + \; \alpha E_0[v]}$$

Concave!