Key concepts and challenges in quantum chemistry:

Some more details about standard methods

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

Electronic Schrödinger equation

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

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

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

Corresponding *electronic wave function*

unknown!

Electronic Schrödinger equation

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

Electronic Schrödinger equation

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

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

*Cartesian **space** coordinates*
of the ith electron

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

***Spin** coordinate*
of the ith electron

$\sigma_i = \uparrow$ **or** $\downarrow$

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

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

Electronic Hamiltonian
operator

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{1}{2}\underbrace{\nabla^2_{\mathbf{r}_i}} + v_{\mathrm{ne}}(\mathbf{r}_i)\times\right) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times$$

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

Kinetic energy
of the ith electron

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{1}{2}\underbrace{\nabla^2_{\mathbf{r}_i}} + \underbrace{v_{\mathrm{ne}}(\mathbf{r}_i)} \times\right) + \frac{1}{2}\sum_{i\neq j}^{N}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}\times$$

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ith electron - nuclei
attraction energy

Electronic Schrödinger equation

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

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

ith electron - nuclei
attraction energy

ith electron - jth electron
repulsion energy

Dirac notation and scalar product

$$\left\{\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \overrightarrow{\Psi} \overset{notation}{=} |\Psi\rangle$$

Dirac notation and scalar product

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“Ket Ψ”

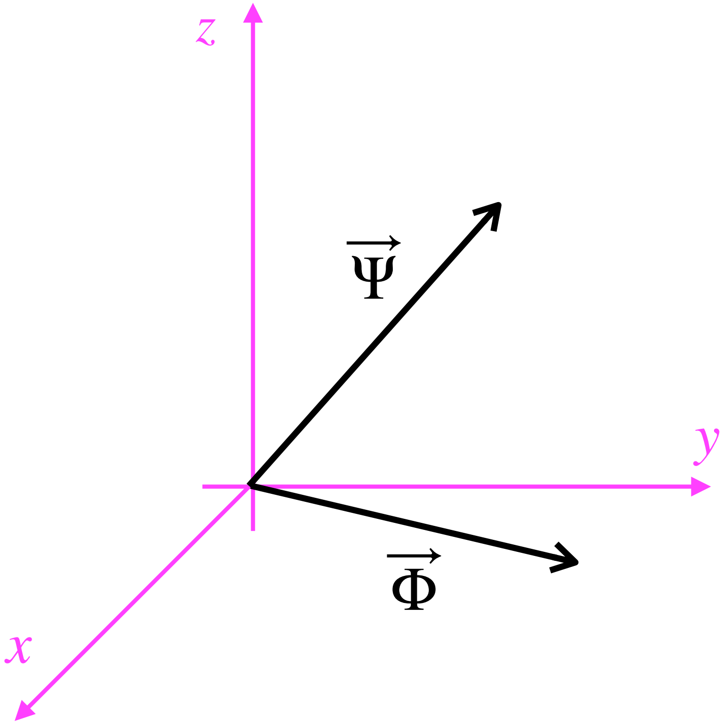
Dirac notation and scalar product

$$\left\{\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \overrightarrow{\Psi} \overset{notation}{=} |\Psi\rangle$$

$$\left\{\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \overrightarrow{\Phi} \overset{notation}{=} |\Phi\rangle$$

“Ket Φ”

Scalar product in real space



$$\vec{\Phi}\,.\,\vec{\Psi} = \Phi_x\Psi_x + \Phi_y\Psi_y + \Phi_z\Psi_z$$

Scalar product of two wave functions

$$\Big\{\Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\Big\} \equiv \overrightarrow{\Psi} \overset{notation}{=} |\Psi\rangle$$

$$\Big\{\Phi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\Big\} \equiv \overrightarrow{\Phi} \overset{notation}{=} |\Phi\rangle$$

$$\overrightarrow{\Phi}\,.\,\overrightarrow{\Psi} \overset{notation}{=} \langle\Phi|\Psi\rangle$$

$$= \int d\mathbf{x}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \; \Phi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N) \times \Psi(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$$

Scalar product of two wave functions

$$\left\{\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \overrightarrow{\Psi} \overset{notation}{=} |\Psi\rangle$$

$$\left\{\Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \overrightarrow{\Phi} \overset{notation}{=} |\Phi\rangle$$

$$\overrightarrow{\Phi} \,.\, \overrightarrow{\Psi} \overset{notation}{=} \langle\Phi|\Psi\rangle = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N \; \Phi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) \times \Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$$

The **square norm** of $|\Psi\rangle$ is therefore denoted as $\overrightarrow{\Psi} \,.\, \overrightarrow{\Psi} \overset{notation}{=} \langle\Psi|\Psi\rangle$

Schrödinger equation in Dirac notations

$$\left\{\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv |\Psi\rangle$$

$$\left\{\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \hat{H}|\Psi\rangle$$

Schrödinger equation in Dirac notations

$$\left\{\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv |\Psi\rangle$$

$$\left\{\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)\right\} \equiv \hat{H}|\Psi\rangle$$

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

Energy evaluation via a scalar product

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

$$\langle\Psi_I|\hat{H}|\Psi_I\rangle = E_I\langle\Psi_I|\Psi_I\rangle$$

Energy evaluation via a scalar product

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

$$\underleftarrow{\langle\Psi_I|\hat{H}|\Psi_I\rangle} = E_I\underleftarrow{\langle\Psi_I|\Psi_I\rangle}$$

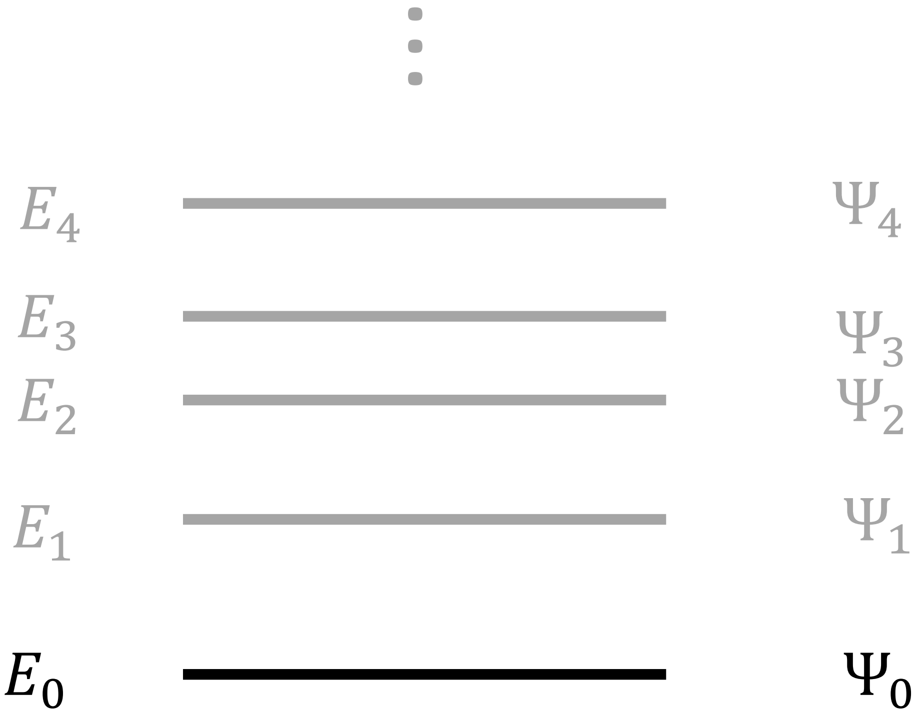
Energy evaluation via a scalar product

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

$$\langle\Psi_I|\hat{H}|\Psi_I\rangle = E_I\langle\Psi_I|\Psi_I\rangle$$

$$E_I = \frac{\langle\Psi_I|\hat{H}|\Psi_I\rangle}{\langle\Psi_I|\Psi_I\rangle}$$

Schrödinger equation for the *ground* state



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

Rayleigh-Ritz variational principle

Theorem: For any *trial* wave function Ψ, we have

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

Rayleigh-Ritz variational principle

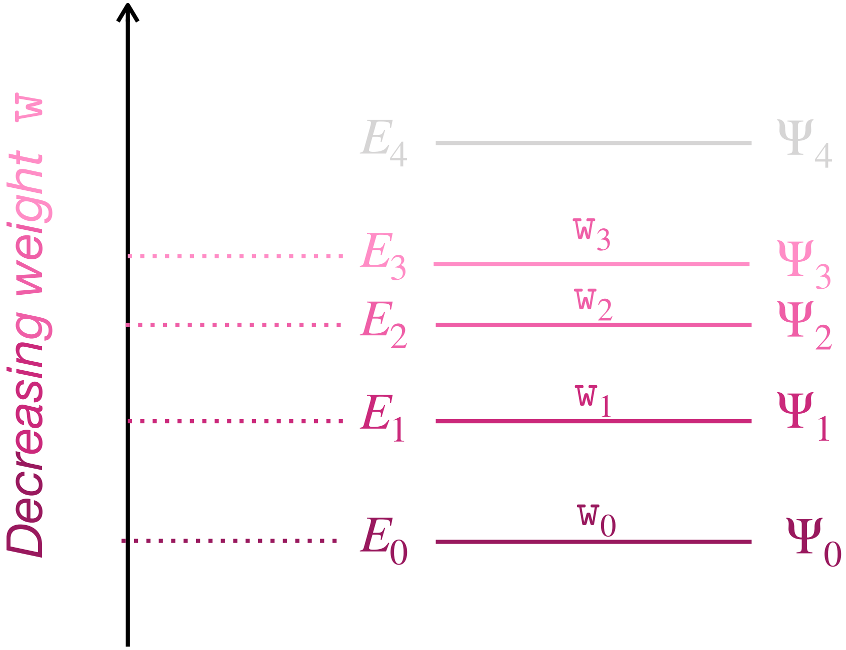
Theorem: For any *trial* wave function Ψ, we have

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

$$\Updownarrow$$

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

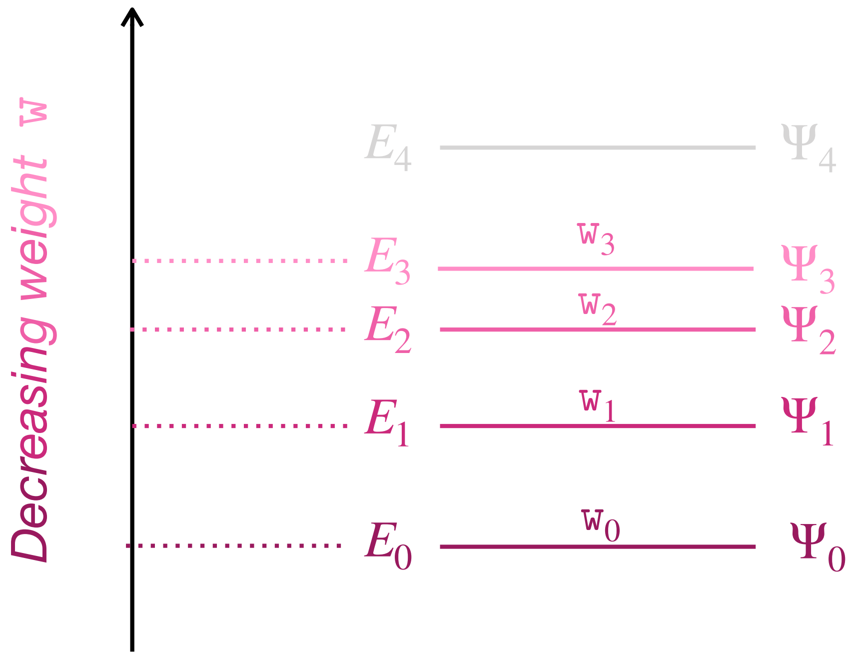
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$\mathtt{w}_0 \frac{\langle\tilde{\Psi}_0|\hat{H}|\tilde{\Psi}_0\rangle}{\langle\tilde{\Psi}_0|\tilde{\Psi}_0\rangle}+\mathtt{w}_1 \frac{\langle\tilde{\Psi}_1|\hat{H}|\tilde{\Psi}_1\rangle}{\langle\tilde{\Psi}_1|\tilde{\Psi}_1\rangle}+\ldots+\mathtt{w}_M \frac{\langle\tilde{\Psi}_M|\hat{H}|\tilde{\Psi}_M\rangle}{\langle\tilde{\Psi}_M|\tilde{\Psi}_M\rangle} \geq \mathtt{w}_0 E_0+\mathtt{w}_1 E_1+\ldots+\mathtt{w}_M E_M$$

A. K. Theophilou, J. Phys. C: Solid State Phys. ***12****, 5419 (1979).*
A. K. Theophilou, in The Single Particle Density in Physics and Chemistry, edited by N. H. March and B. M. Deb (Academic Press, 1987), pp. 210–212.
E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2805 (1988).*
E. K. U. Gross, L. N. Oliveira, and W. Kohn, Phys. Rev. A ***37****, 2809 (1988).*
L. N. Oliveira, E. K. U. Gross, and W. Kohn, Phys. Rev. A ***37****, 2821 (1988).*

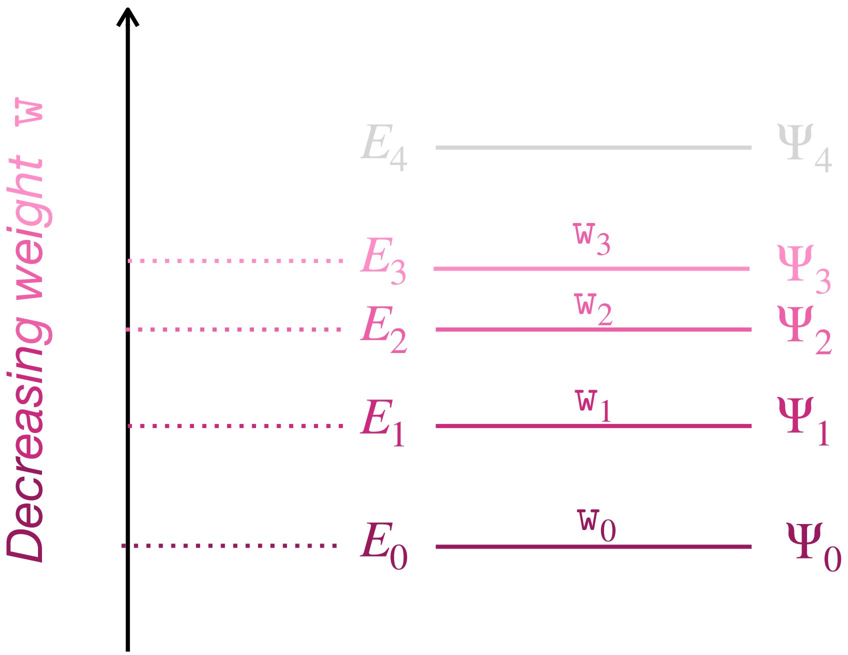
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$\mathtt{w}_0 \frac{\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle} + \mathtt{w}_1 \frac{\langle \tilde{\Psi}_1 | \hat{H} | \tilde{\Psi}_1 \rangle}{\langle \tilde{\Psi}_1 | \tilde{\Psi}_1 \rangle} + \ldots + \mathtt{w}_M \frac{\langle \tilde{\Psi}_M | \hat{H} | \tilde{\Psi}_M \rangle}{\langle \tilde{\Psi}_M | \tilde{\Psi}_M \rangle} \geq \mathtt{w}_0 E_0 + \mathtt{w}_1 E_1 + \ldots + \mathtt{w}_M E_M$$

Arbitrary **ordered positive weights**

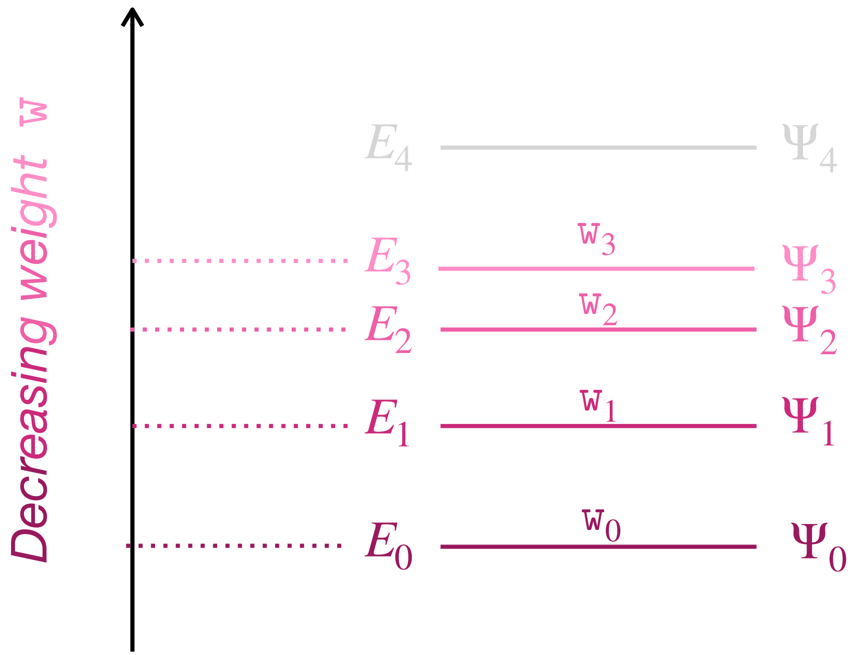
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$\mathtt{w}_0 \frac{\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle} + \mathtt{w}_1 \frac{\langle \tilde{\Psi}_1 | \hat{H} | \tilde{\Psi}_1 \rangle}{\langle \tilde{\Psi}_1 | \tilde{\Psi}_1 \rangle} + \ldots + \mathtt{w}_M \frac{\langle \tilde{\Psi}_M | \hat{H} | \tilde{\Psi}_M \rangle}{\langle \tilde{\Psi}_M | \tilde{\Psi}_M \rangle} \geq \mathtt{w}_0 E_0 + \mathtt{w}_1 E_1 + \ldots + \mathtt{w}_M E_M$$

Orthogonal **trial** wave functions

Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



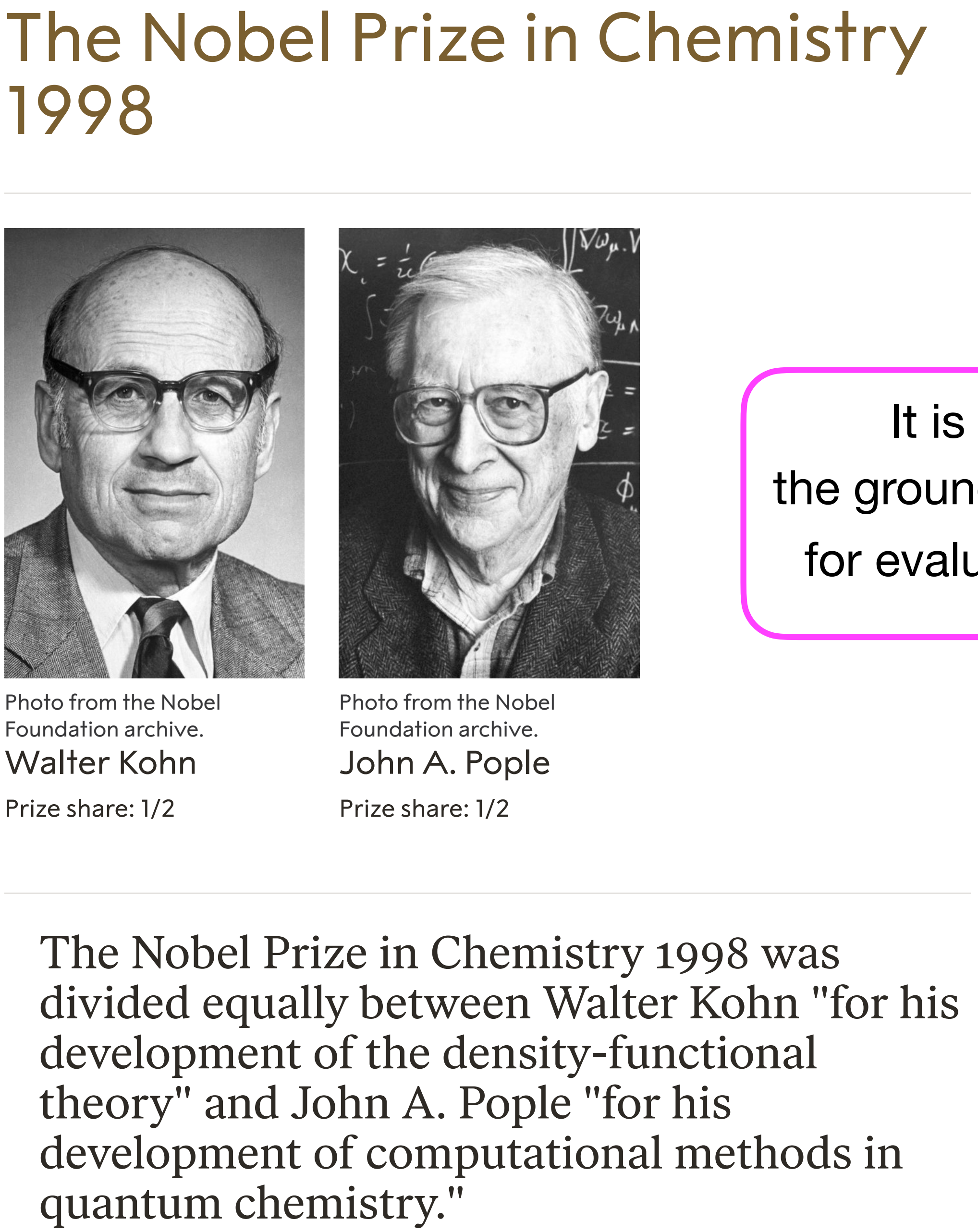
$$\mathtt{w}_0 \frac{\langle\tilde{\Psi}_0|\hat{H}|\tilde{\Psi}_0\rangle}{\langle\tilde{\Psi}_0|\tilde{\Psi}_0\rangle} + \mathtt{w}_1 \frac{\langle\tilde{\Psi}_1|\hat{H}|\tilde{\Psi}_1\rangle}{\langle\tilde{\Psi}_1|\tilde{\Psi}_1\rangle} + \ldots + \mathtt{w}_M \frac{\langle\tilde{\Psi}_M|\hat{H}|\tilde{\Psi}_M\rangle}{\langle\tilde{\Psi}_M|\tilde{\Psi}_M\rangle} \geq \mathtt{w}_0 E_0 + \mathtt{w}_1 E_1 + \ldots + \mathtt{w}_M E_M$$

Desired M lowest excited-state energies

Density-functional theory (DFT)

$$n$$

Density-functional theory (DFT)



The Nobel Prize in Chemistry 1998

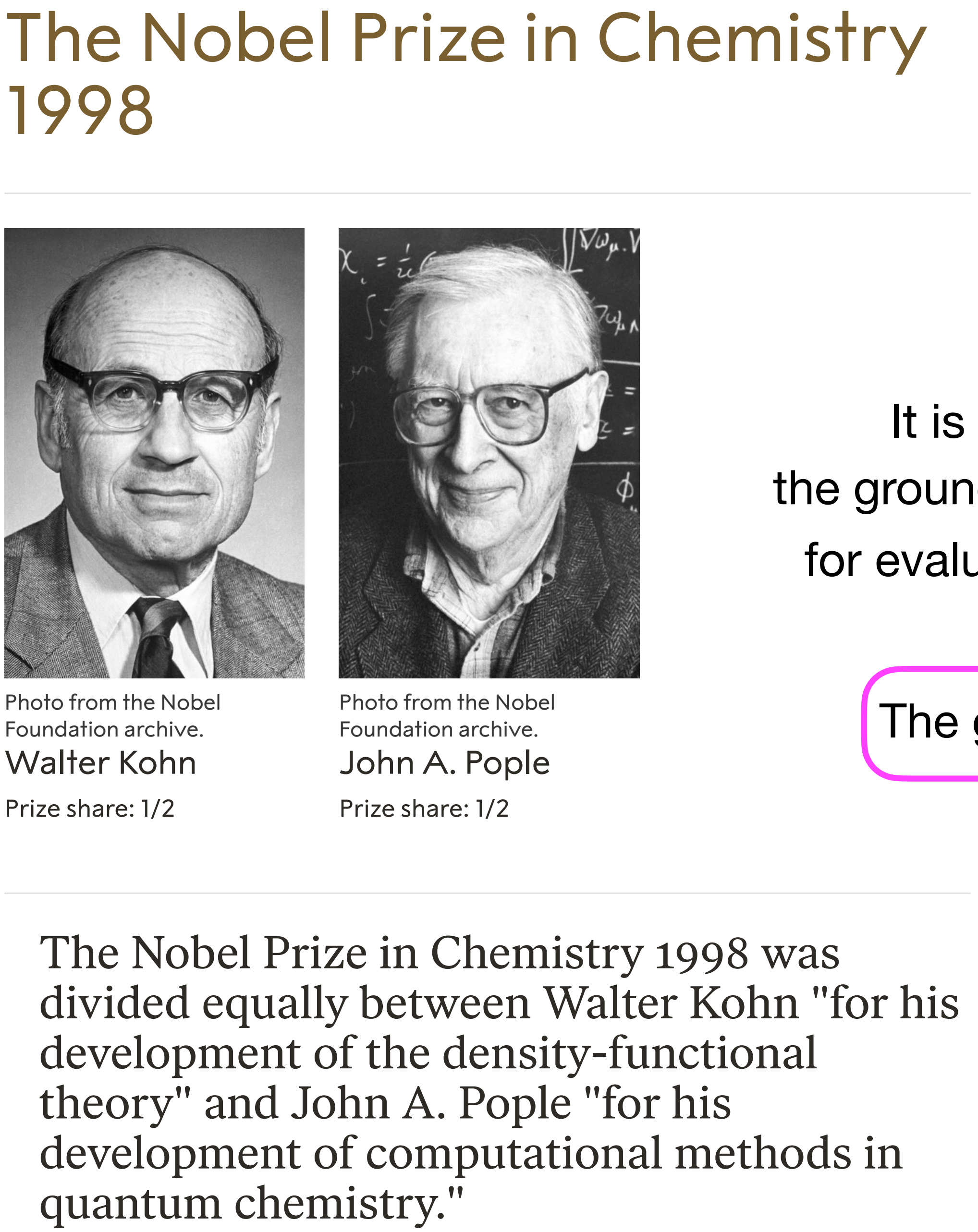
Photo from the Nobel Foundation archive.
Walter Kohn
Prize share: 1/2

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

Density-functional theory (DFT)

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.***

$$\boxed{n_\Psi(\mathbf{x}) = N\int d\mathbf{x}_2 \ldots \int d\mathbf{x}_N\,|\Psi(\mathbf{x}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2} \xrightarrow{\Psi = \Psi_0} n_{\Psi_0}(\mathbf{x})$$

Levy's constrained search formalism

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

Levy's constrained search formalism

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

We use **normalized** wave functions for convenience, *i.e.*, $\langle \Psi | \Psi \rangle = 1$.

Levy's constrained search formalism

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

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

$\downarrow$

Pre-minimisation over wave functions $\mathbf{\Psi}$
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

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

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

Minimisation over ***densities*** n

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

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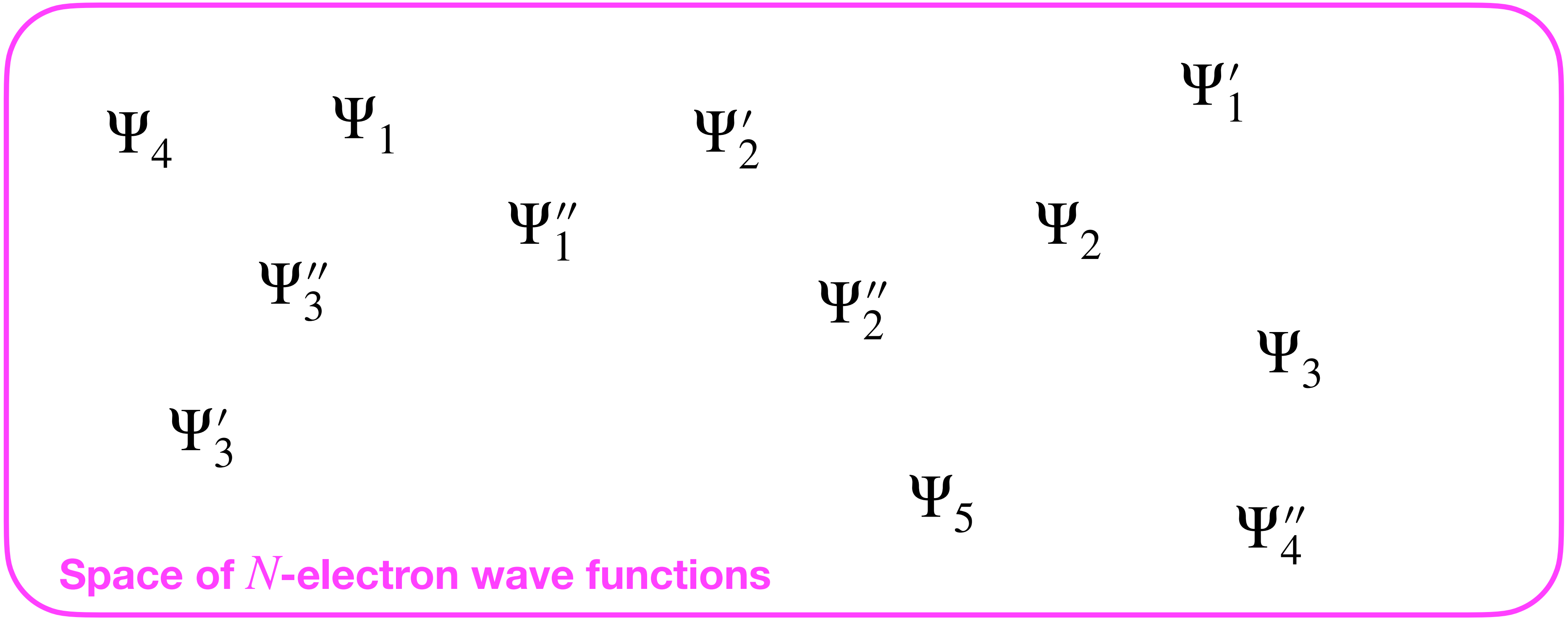
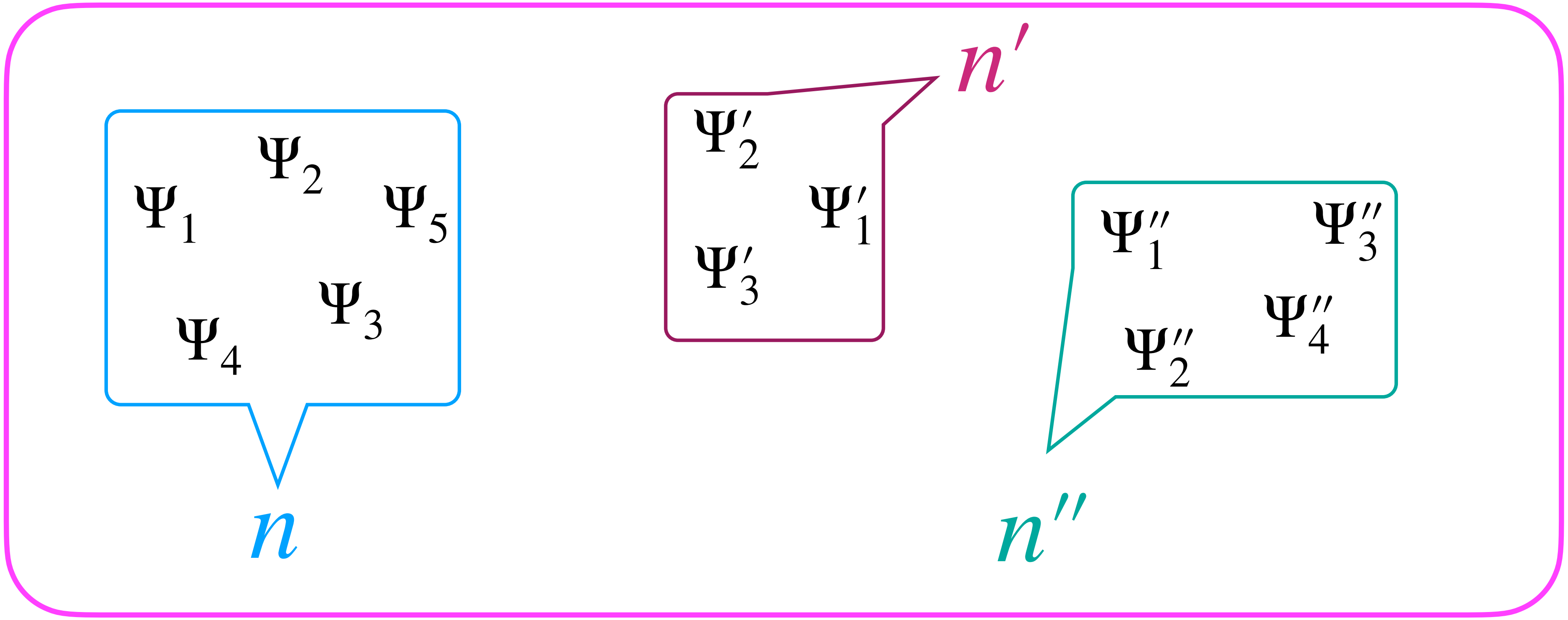


Levy M (1979) Proc Natl Acad Sci USA ***76****(12):6062*

Levy's constrained search formalism

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

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



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

Levy's constrained search formalism

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

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

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

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

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

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

Levy's constrained search formalism

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

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

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

Electrons-nuclei ***attraction energy***

Levy's constrained search formalism

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

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Levy's constrained search formalism

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

Levy's constrained search formalism

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

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

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

Levy's constrained search formalism

$$\boxed{E_0 = \min_{n} \left\{ F[n] + \int d\mathbf{r}\, v_{\mathrm{ne}}(\mathbf{r}) n(\mathbf{r}) \right\}}$$

Universal **Hohenberg-Kohn density functional**

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

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

Kohn-Sham DFT formalism

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

Interacting universal functional

Non-interacting
(kinetic energy) functional

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

Kohn-Sham DFT formalism

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

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

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

Interacting universal functional

Non-interacting
(kinetic energy) functional

$$F[n] - T_{\mathrm{s}}[n] = \underbrace{E_{\mathrm{Hxc}}[n]}_{\substack{\textbf{Universal many-electron} \\ \textit{Hartree-exchange-correlation functional}}}$$

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

Kohn-Sham DFT formalism

Holy grail of DFT

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

Universal many-electron
Hartree-exchange-correlation functional

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

Kohn-Sham DFT formalism

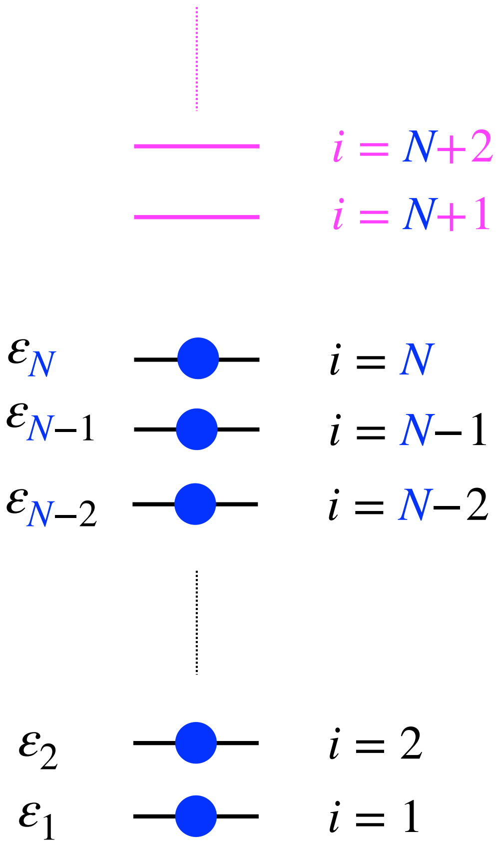
*The **exact** xc functional is **uniquely defined** but*
many** (many) **approximations
can be found in the literature (LDA, PBE, B3LYP, SCAN, …)

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

Universal many-electron
Hartree-exchange-correlation functional

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

One-electron Kohn-Sham DFT equations



$i = N+2$

$i = N+1$

ε_N $i = N$

ε_{N-1} $i = N-1$

ε_{N-2} $i = N-2$

ε_2 $i = 2$

ε_1 $i = 1$

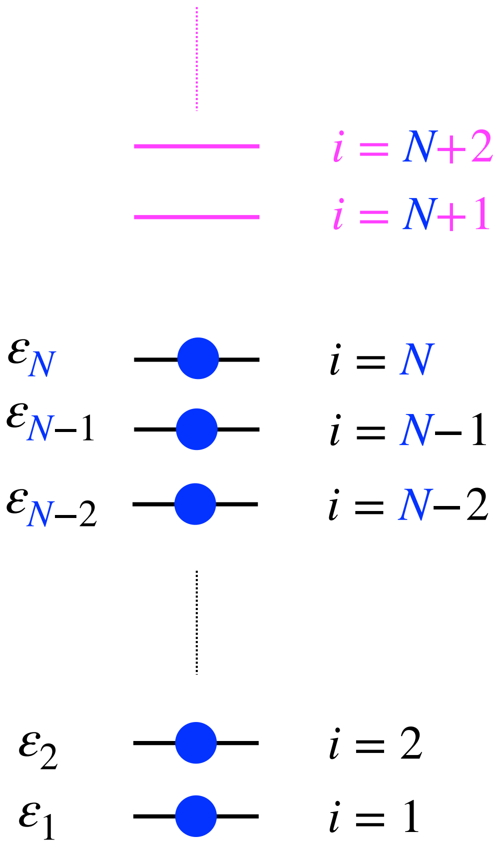
$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2}+\left(v_{\mathrm{ne}}(\mathbf{r})+\frac{\delta E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r})}\right)\times\right]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$

KS orbitals

One-electron energy levels

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

One-electron Kohn-Sham DFT equations



One-electron energy levels

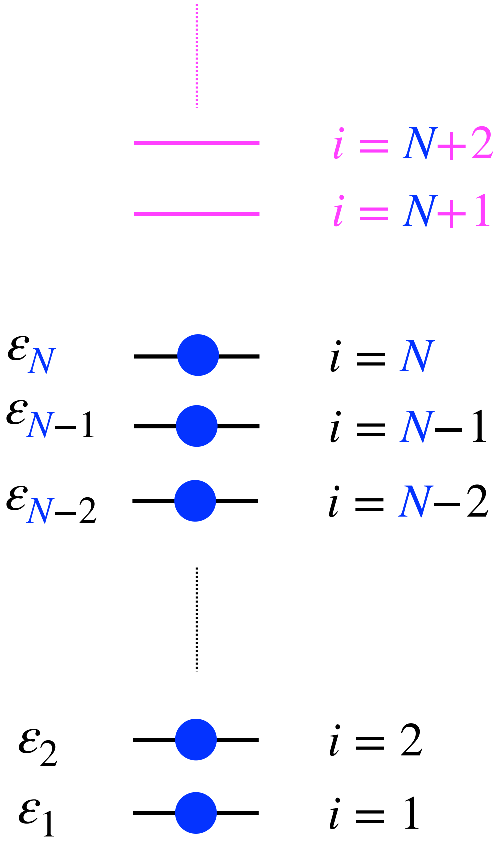
$$\left[-\frac{\nabla^2_{\mathbf{r}}}{2}+\left(v_{\mathrm{ne}}(\mathbf{r})+\frac{\delta E_{\mathrm{Hxc}}[n_0]}{\delta n(\mathbf{r})}\right)\times\right]\varphi_i(\mathbf{r})=\varepsilon_i\varphi_i(\mathbf{r})$$

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

Exact density

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

One-electron Kohn-Sham DFT equations



One-electron energy levels

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

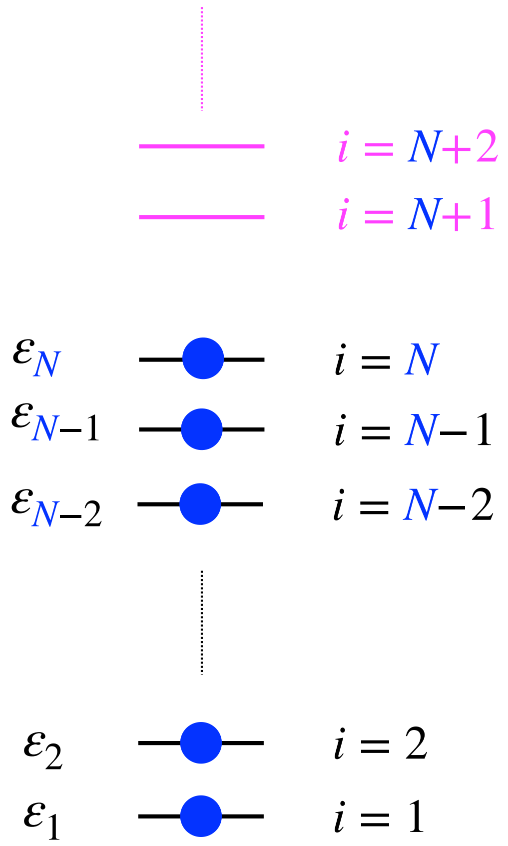
$$n_0(\mathbf{r}) = \sum_{i=1}^{N}|\varphi_i(\mathbf{r})|^2$$

Exact density

Exactification of the one-electron picture

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

One-electron Kohn-Sham DFT equations



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Implicit description of electron correlation

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Exact density

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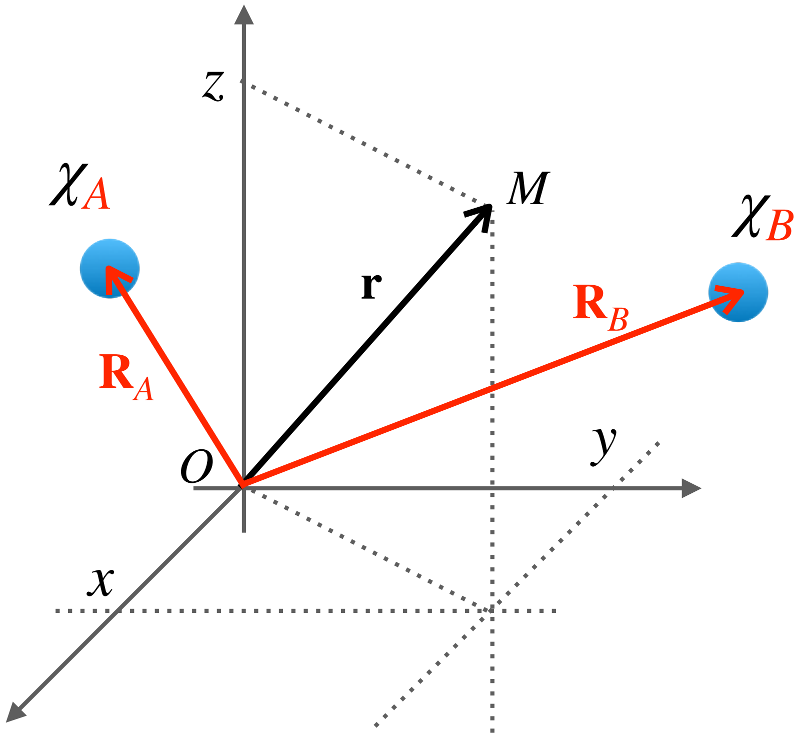
Construction of Kohn-Sham DFT molecular orbitals

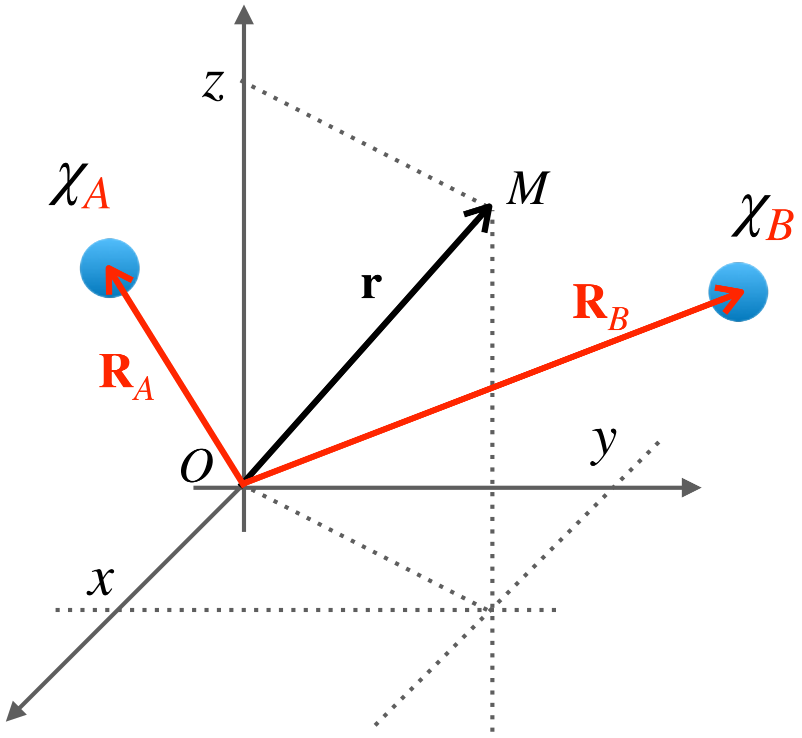


Atomic orbitals

(basis set)

$$\varphi_p(\mathbf{r}) = C_{Ap}\,\chi_A(\mathbf{r}) + C_{Bp}\,\chi_B(\mathbf{r})$$

Construction of Kohn-Sham DFT molecular orbitals



$$\varphi_p(\mathbf{r}) = C_{Ap}\,\chi_A(\mathbf{r}) + C_{Bp}\,\chi_B(\mathbf{r})$$

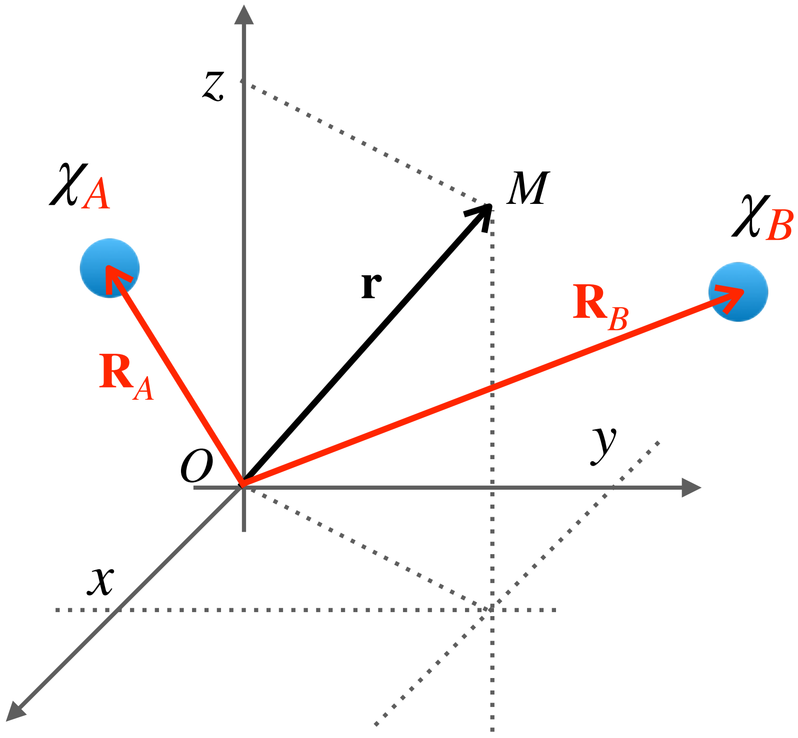
$$\overset{notation}{\equiv} \sum_{\mu=1}^{\mathscr{M}} C_{\mu p}\chi_\mu(\mathbf{r})$$

$\uparrow$

Atomic orbitals

(basis set)

Construction of Kohn-Sham DFT molecular orbitals



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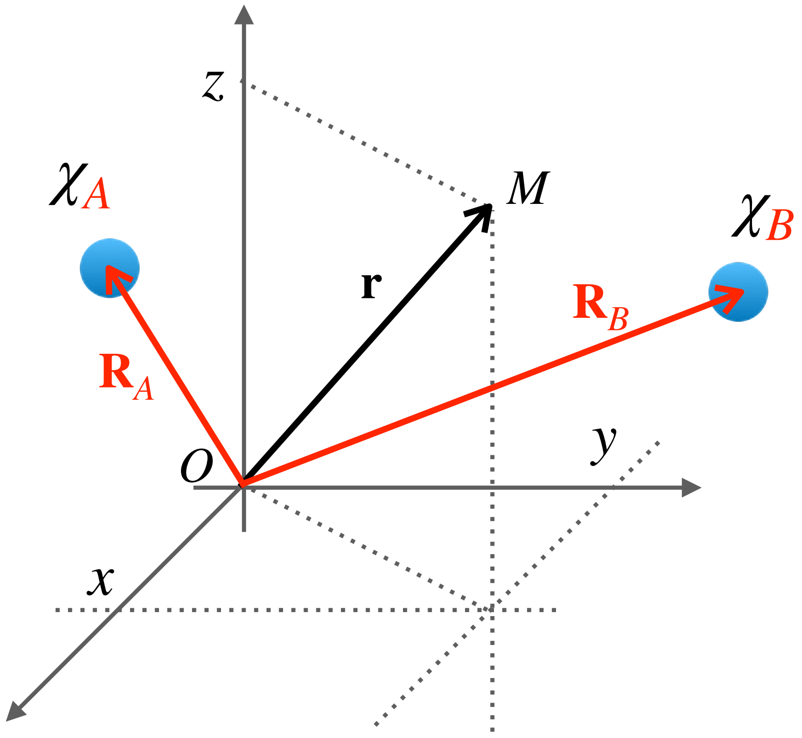
$$\overset{notation}{\equiv} \sum_{\mu=1}^{\mathscr{M}} \boxed{C_{\mu p}}\,\chi_\mu(\mathbf{r})$$

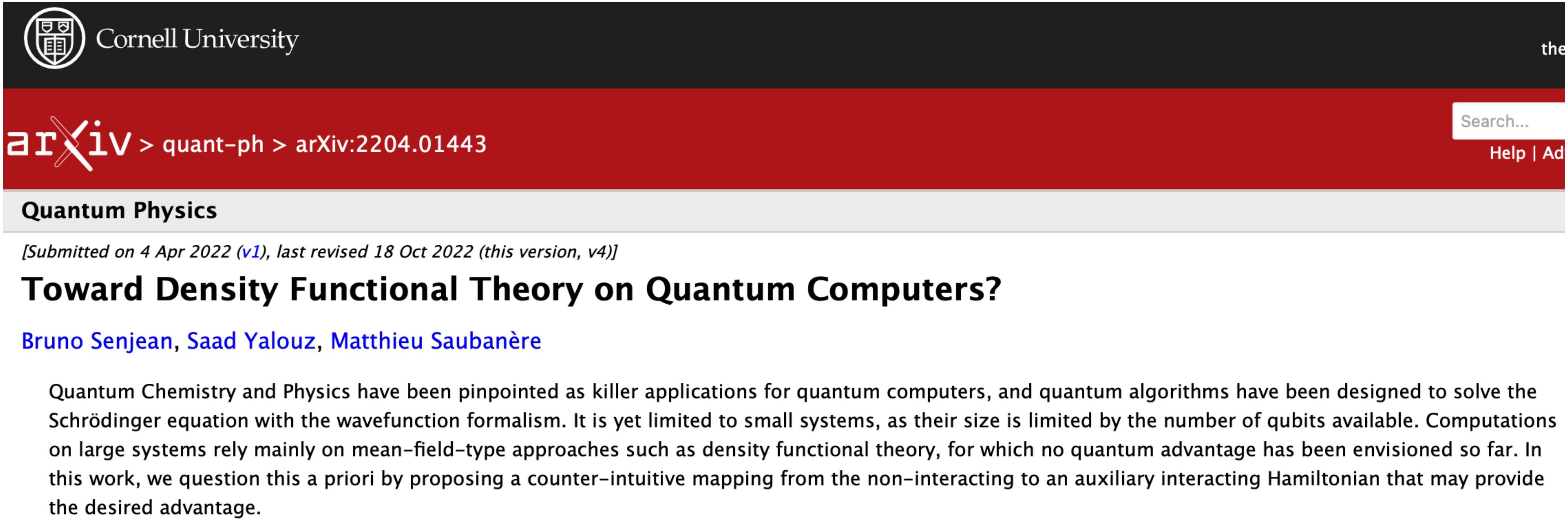
To-be-optimized
molecular orbital coefficients

Construction of Kohn-Sham DFT molecular orbitals



Size of the atomic orbital basis

$$\varphi_p(\mathbf{r}) = \sum_{\mu=1}^{\mathscr{M}} C_{\mu p}\, \chi_\mu(\mathbf{r})$$



arXiv > quant-ph > arXiv:2204.01443

Quantum Physics

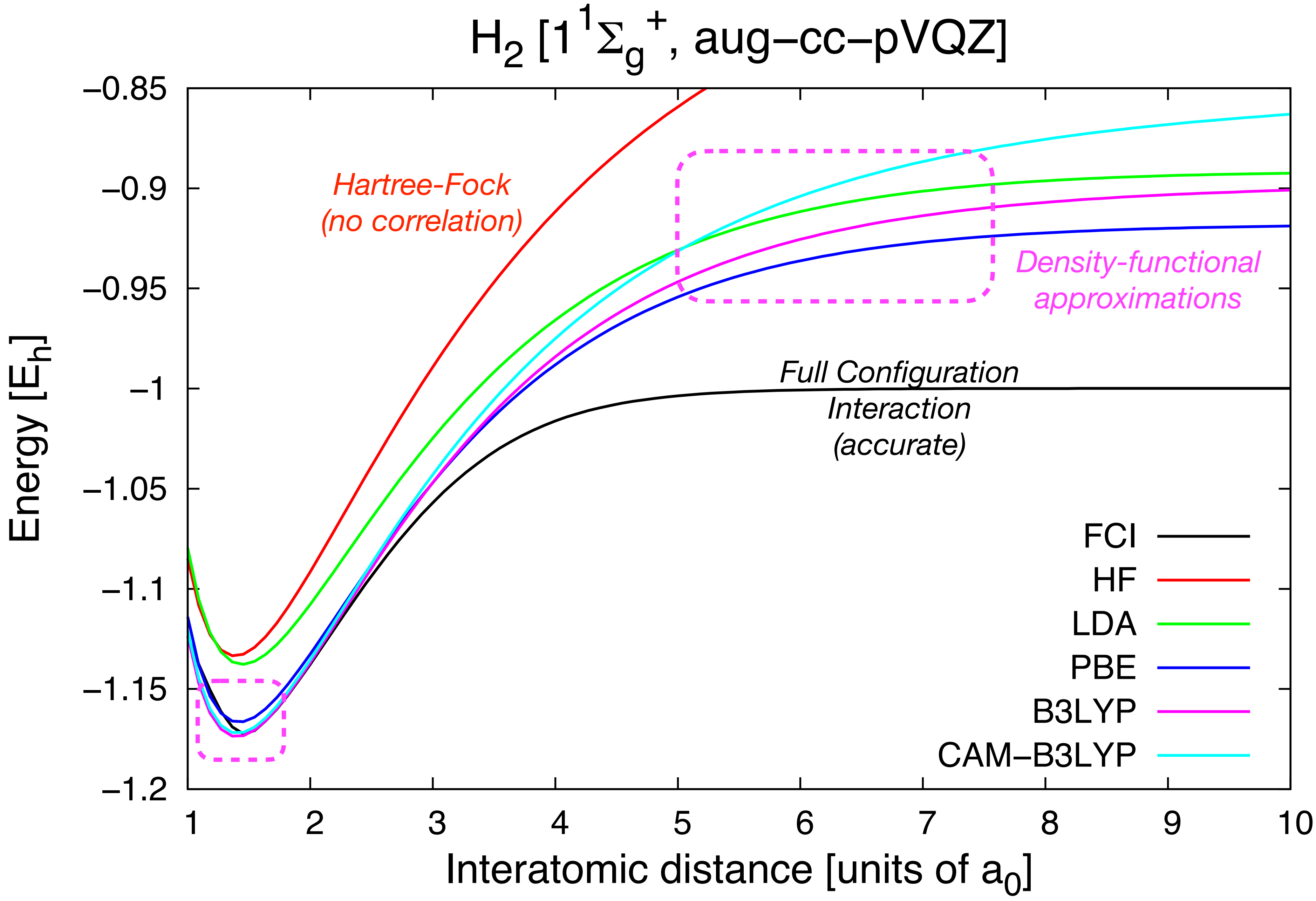
[Submitted on 4 Apr 2022 (v1), last revised 18 Oct 2022 (this version, v4)]

Toward Density Functional Theory on Quantum Computers?

Bruno Senjean, Saad Yalouz, Matthieu Saubanère

Quantum Chemistry and Physics have been pinpointed as killer applications for quantum computers, and quantum algorithms have been designed to solve the Schrödinger equation with the wavefunction formalism. It is yet limited to small systems, as their size is limited by the number of qubits available. Computations on large systems rely mainly on mean-field-type approaches such as density functional theory, for which no quantum advantage has been envisioned so far. In this work, we question this a priori by proposing a counter-intuitive mapping from the non-interacting to an auxiliary interacting Hamiltonian that may provide the desired advantage.

Success and failures of density-functional approximations



PCCP

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PERSPECTIVE

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Cite this: DOI: 10.1039/d2cp02827a

DFT exchange: sharing perspectives on the workhorse of quantum chemistry and materials science

Andrew M. Teale, *[a] Trygve Helgaker, *[b] Andreas Savin, *[c] Carlo Adamo, [d] Bálint Aradi, [e] Alexei V. Arbuznikov, [f] Paul W. Ayers, [g] Evert Jan Baerends, [h] Vincenzo Barone, [i] Patrizia Calaminici, [j] Eric Cancès, [k] Emily A. Carter, [l] Pratim Kumar Chattaraj, [m] Henry Chermette, [n] Ilaria Ciofini, [d] T. Daniel Crawford, [op] Frank De Proft, [q] John F. Dobson, [r] Claudia Draxl, [st] Thomas Frauenheim,[euv] Emmanuel Fromager, [w] Patricio Fuentealba, [x] Laura Gagliardi, [y] Giulia Galli, [z] Jiali Gao, [aaab] Paul Geerlings, [q] Nikitas Gidopoulos, [ac] Peter M. W. Gill, [ad] Paola Gori-Giorgi, [ae] Andreas Görling, [af] Tim Gould, [ag] Stefan Grimme, [ah] Oleg Gritsenko, [ae] Hans Jørgen Aagaard Jensen, [ai] Erin R. Johnson, [aj] Robert O. Jones, [ak] Martin Kaupp, [f] Andreas M. Köster, [j] Leeor Kronik, [al] Anna I. Krylov, [am] Simen Kvaal, [b] Andre Laestadius, [b] Mel Levy, [an] Mathieu Lewin, [ao] Shubin Liu, [apaq] Pierre-François Loos, [ar] Neepa T. Maitra, [as] Frank Neese, [at] John P. Perdew, [au] Katarzyna Pernal, [av] Pascal Pernot, [aw] Piotr Piecuch, [axay] Elisa Rebolini, [az] Lucia Reining, [babb] Pina Romaniello, [bc] Adrienn Ruzsinszky, [bd] Dennis R. Salahub, [be] Matthias Scheffler, [bf] Peter Schwerdtfeger, [bg] Viktor N. Staroverov, [bh] Jianwei Sun, [bi] Erik Tellgren, [b] David J. Tozer, [bj] Samuel B. Trickey, [bk] Carsten A. Ullrich, [bl] Alberto Vela, [j] Giovanni Vignale, [bm] Tomasz A. Wesolowski, [bn] Xin Xu [bo] and Weitao Yang [bp]

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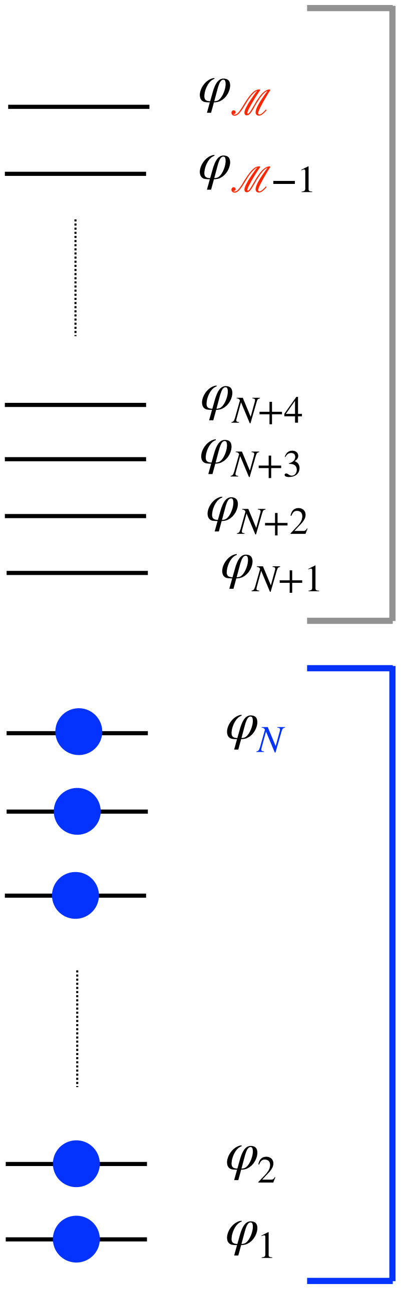
rsc.li/pccp

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.

Wave function theory

$$\Psi$$

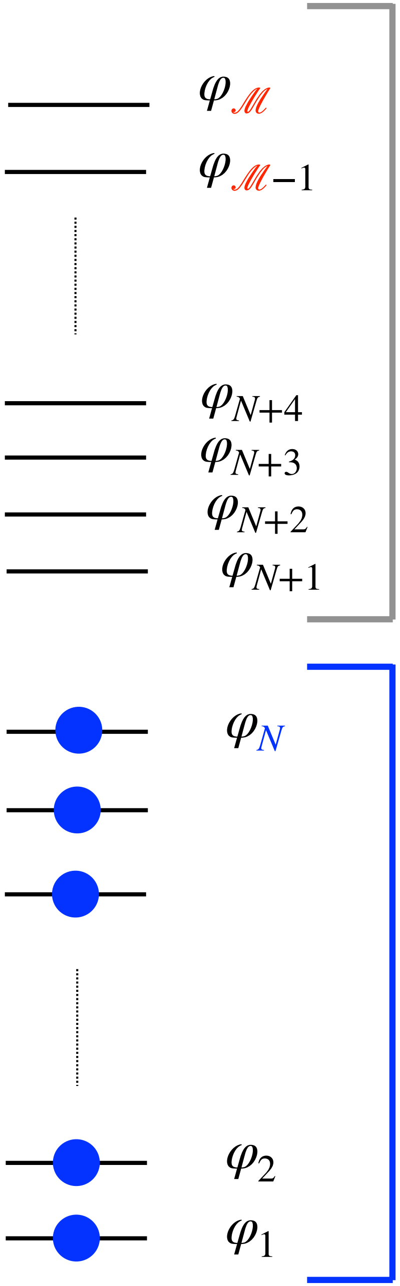
Explicit description of electron correlation



Virtual orbitals

Reference ground-state configuration
(the one used in KS-DFT)

Explicit description of electron correlation



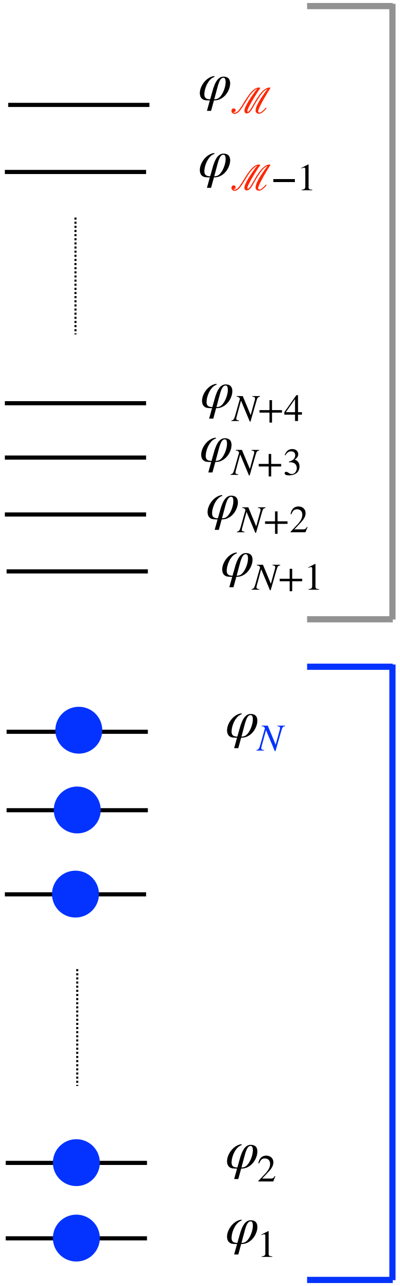
Virtual orbitals

Creation operators

$$|\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\text{vac}\rangle$$

Second-quantized notation

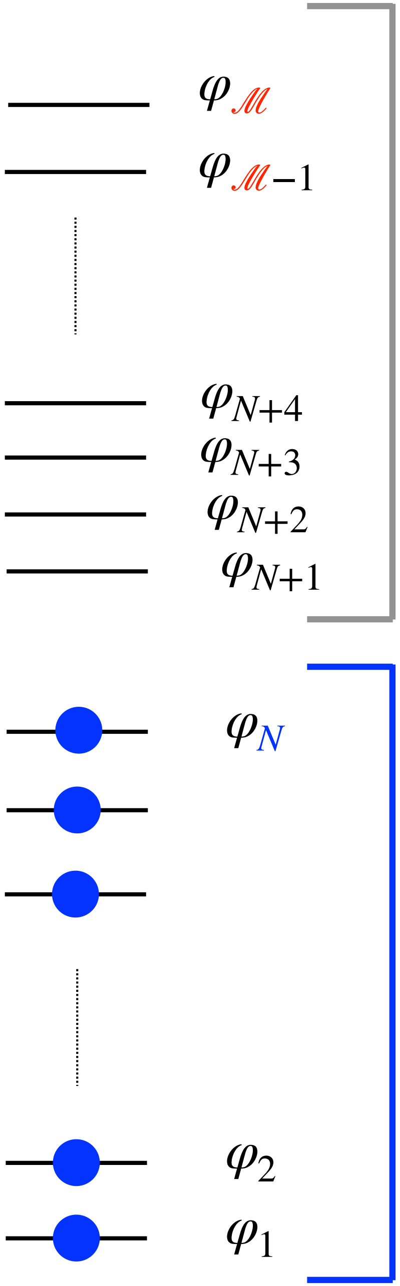
Explicit description of electron correlation



Virtual orbitals

$$|\Phi_0\rangle \equiv \underleftarrow{\hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\mathrm{vac}\rangle}$$

Explicit description of electron correlation

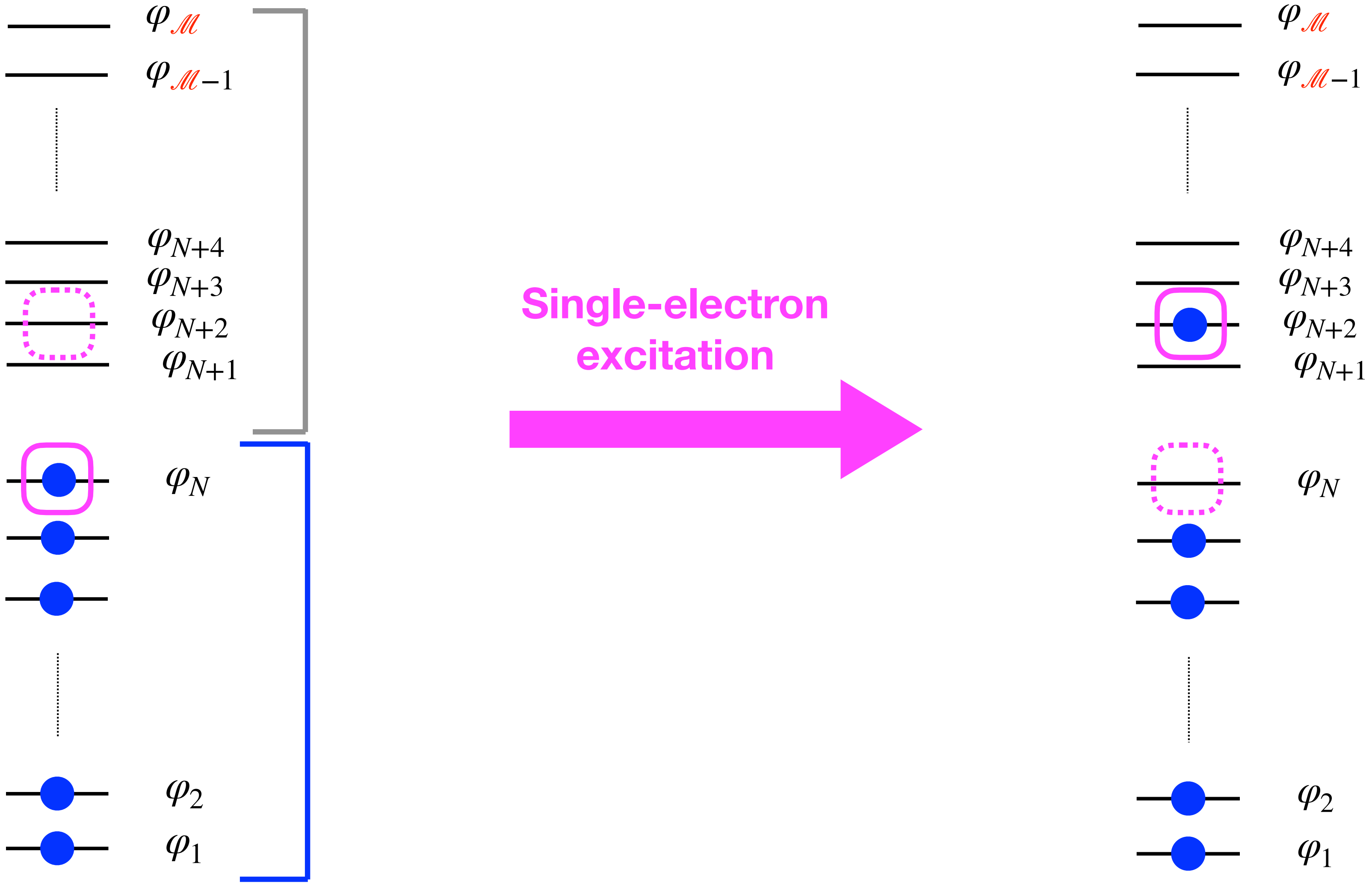


Virtual orbitals

$$|\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\mathrm{vac}\rangle$$

Reference **Slater determinant**

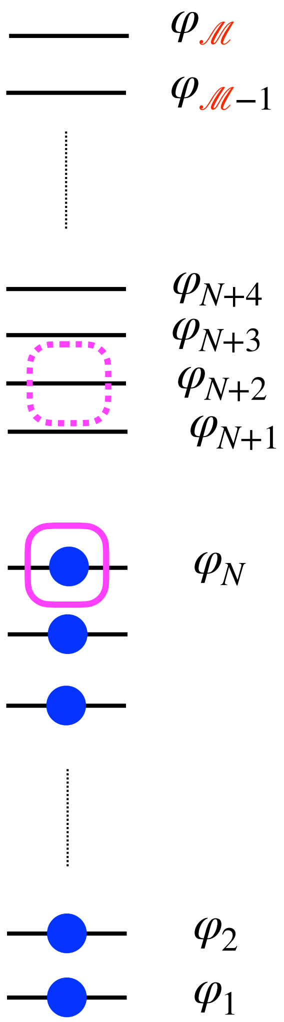
Explicit description of electron correlation



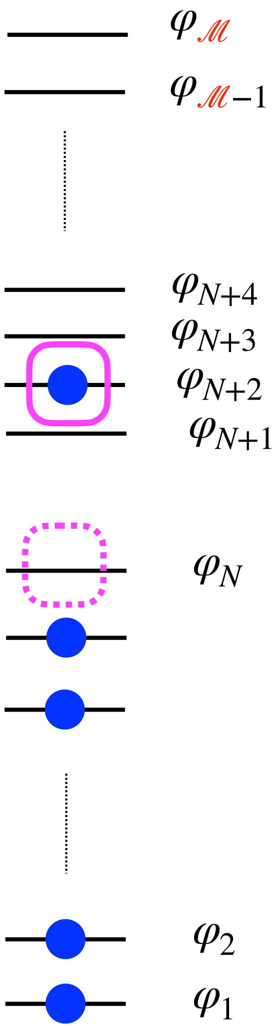
Single-electron excitation

$$|\Phi_0\rangle$$

Explicit description of electron correlation



$$|\Phi_0\rangle$$

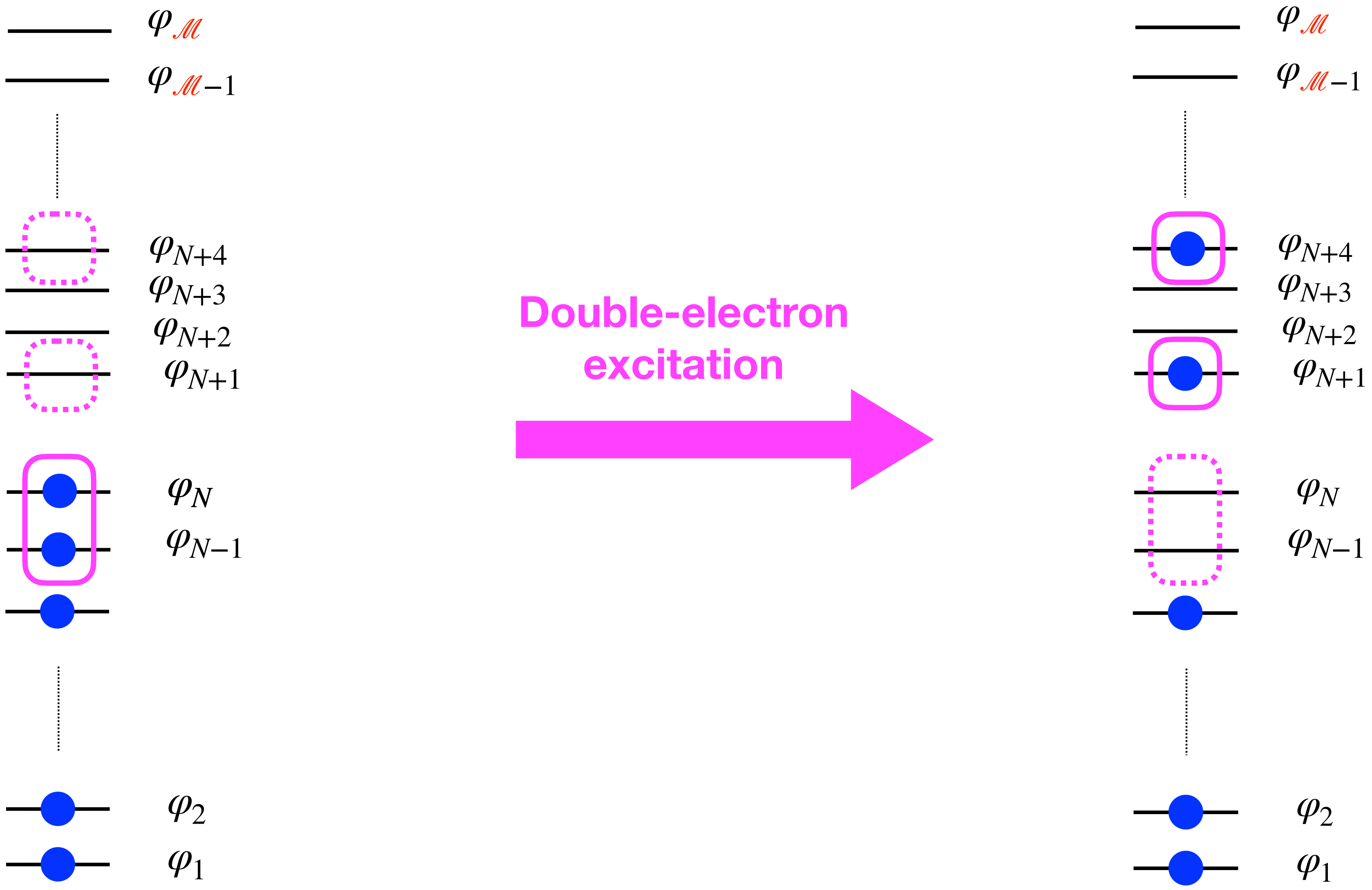


Annihilation operator

$$\hat{a}^\dagger_{N+2}\hat{a}_N|\Phi_0\rangle$$

Second-quantized notation

Explicit description of electron correlation

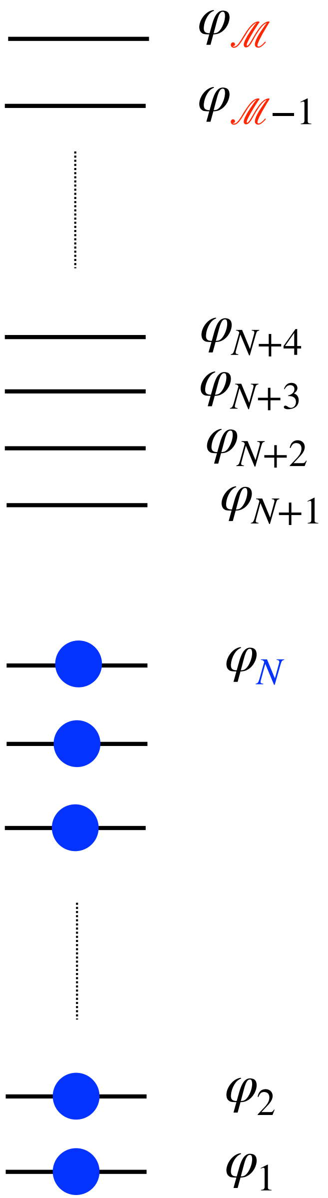


Double-electron excitation

$$|\Phi_0\rangle$$

$$\hat{a}^{\dagger}_{N+4}\hat{a}^{\dagger}_{N+1}\hat{a}_{N-1}\hat{a}_{N}|\Phi_0\rangle$$

Explicit description of electron correlation



Triples, quadruples, …, N-tuples →

Configuration Interaction (CI) method

$$|\Psi_0\rangle \approx \hat{C}\,|\Phi_0\rangle$$

Excitation operator

Configuration Interaction (CI) method

$$|\Psi_0\rangle \approx \hat{C}\,|\Phi_0\rangle$$

$$\hat{C} = C_0 + \sum_{a=N+1}^{\mathcal{M}} \sum_{i=1}^{N} C_i^a \underbrace{\hat{a}_a^\dagger \hat{a}_i}_{\textbf{Singles}} + \sum_{a,b=N+1}^{\mathcal{M}} \sum_{i,j=1}^{N} C_{ij}^{ab} \underbrace{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j}_{\textbf{Doubles}} + \sum_{a,b,c=N+1}^{\mathcal{M}} \sum_{i,j,k=1}^{N} C_{ijk}^{abc} \underbrace{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k}_{\textbf{Triples}} + \dots$$

Configuration Interaction (CI) method

$$|\Psi_0\rangle \approx \hat{C}\,|\Phi_0\rangle$$

$$\hat{C} = C_0 + \sum_{a=N+1}^{\mathscr{M}} \sum_{i=1}^{N} C_i^a \,\hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathscr{M}} \sum_{i,j=1}^{N} C_{ij}^{ab} \,\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \sum_{a,b,c=N+1}^{\mathscr{M}} \sum_{i,j,k=1}^{N} C_{ijk}^{abc} \,\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k + \ldots$$

To-be-optimized CI coefficients

Configuration Interaction (CI) method

$$|\Psi_0\rangle \approx \hat{C}|\Phi_0\rangle = \sum_{\xi} C_{\xi}|\mathrm{det}_{\xi}\rangle = |\Psi(\mathbf{C})\rangle$$

$$\hat{C} = C_0 + \sum_{a=N+1}^{\mathscr{M}} \sum_{i=1}^{N} C_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathscr{M}} \sum_{i,j=1}^{N} C_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \sum_{a,b,c=N+1}^{\mathscr{M}} \sum_{i,j,k=1}^{N} C_{ijk}^{abc} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k + \ldots$$

To-be-optimized CI coefficients

Configuration Interaction (CI) method

$$E_{\mathrm{CI}} = \min_{\mathbf{C}} \frac{\langle \Psi(\mathbf{C}) \,|\, \hat{H} \,|\, \Psi(\mathbf{C}) \rangle}{\langle \Psi(\mathbf{C}) \,|\, \Psi(\mathbf{C}) \rangle}$$

$$|\,\Psi(\mathbf{C})\rangle = \sum_{\xi} C_{\xi} \,|\, \mathrm{det}_{\xi} \rangle$$

Configuration Interaction (CI) method

$$E_{\mathrm{CI}} = \min_{\mathbf{C}} \frac{\langle \Psi(\mathbf{C}) | \hat{H} | \Psi(\mathbf{C}) \rangle}{\langle \Psi(\mathbf{C}) | \Psi(\mathbf{C}) \rangle}$$

$$|\Psi(\mathbf{C})\rangle = \sum_{\xi} C_{\xi} |\det_{\xi}\rangle$$

$$\Updownarrow$$

$$\boxed{\begin{matrix} H_{00} & H_{01} & \cdots & H_{0\xi'} & \cdots \\ H_{10} & \cdots & & & \\ \vdots & & & & \\ H_{\xi 0} & \cdots & & H_{\xi\xi'} & \cdots \\ \vdots & & & & \end{matrix}} \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_{\xi} \\ \vdots \end{bmatrix} = E_{\mathrm{CI}} \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_{\xi} \\ \vdots \end{bmatrix}$$

Matrix diagonalization problem

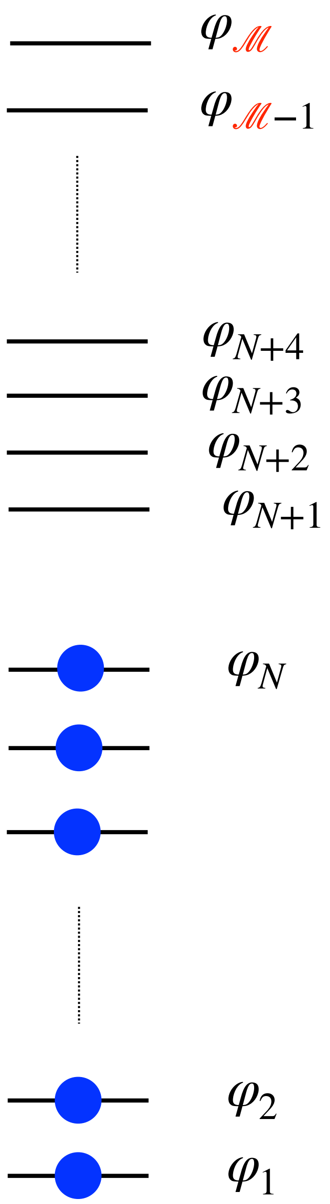
Configuration Interaction (CI) method

$$H_{\xi\xi'} = \langle \mathrm{det}_{\xi} | \hat{H} | \mathrm{det}_{\xi'} \rangle$$

$$\boxed{\begin{matrix} H_{00} & H_{01} & \cdots & H_{0\xi'} & \cdots \\ H_{10} & \cdots & & & \\ \vdots & & & & \\ H_{\xi 0} & \cdots & & H_{\xi\xi'} & \cdots \\ \vdots & & & & \end{matrix}} \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_{\xi} \\ \vdots \end{bmatrix} = E_{\mathrm{CI}} \begin{bmatrix} C_0 \\ C_1 \\ \vdots \\ C_{\xi} \\ \vdots \end{bmatrix}$$

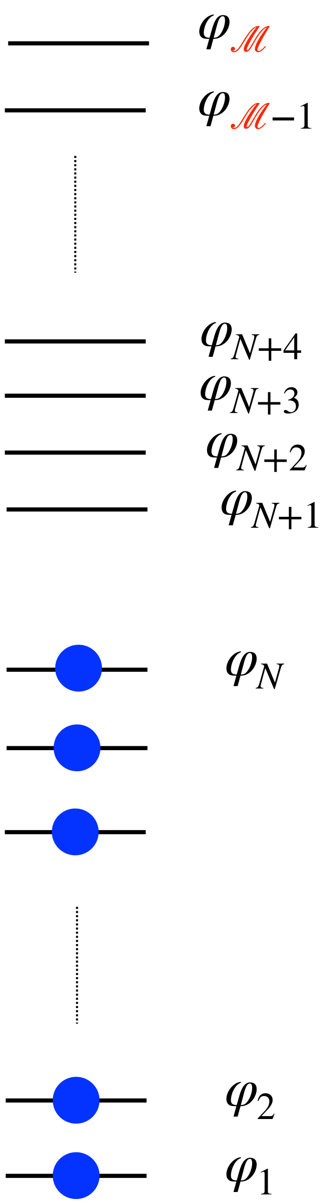
CI Hamiltonian matrix

How many determinants in total *for a full CI (FCI) calculation?*



We have $\mathscr{M}$ (spin-) orbitals available for N electrons

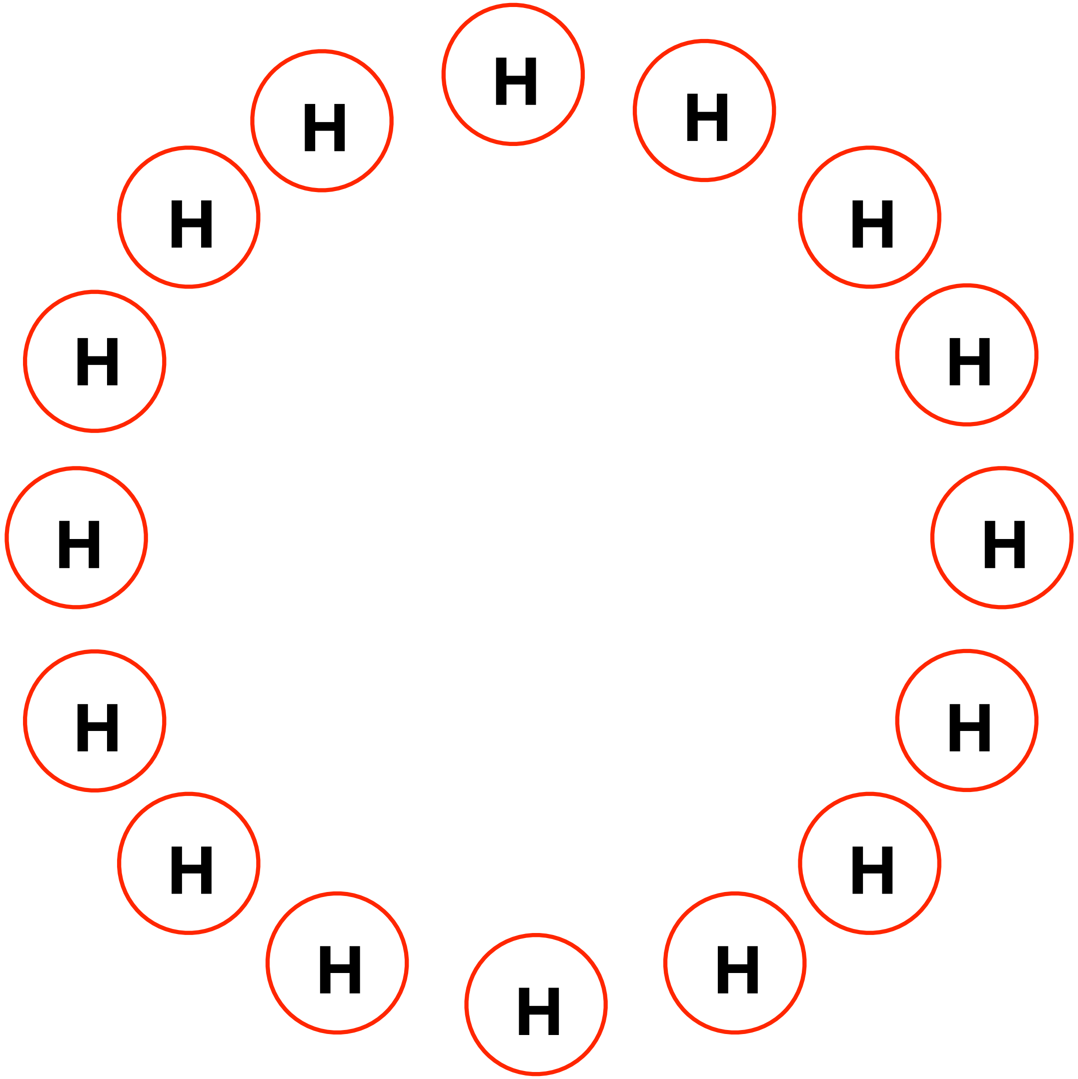
How many determinants in total?



We have $\mathscr{M}$ (spin-) orbitals available for N electrons

$$N_{\text{det.}} = \binom{\mathscr{M}}{N} = \frac{\mathscr{M}\,!}{N!(\mathscr{M}-N)\,!}$$

How many determinants in total?



$$\mathscr{M} = 2 \times N$$

Spin

How many determinants in total?

$$\mathscr{M} = 2 \times N$$

$$N_{\text{det.}} = \frac{\mathscr{M}\,!}{N!(\mathscr{M} - N)\,!} = \frac{(2N)\,!}{(N!)^2}$$

How many determinants in total?

$$\mathcal{M} = 2 \times N$$

$$N_{\text{det.}} = \frac{\mathcal{M}\,!}{N!(\mathcal{M}-N)\,!} = \frac{(2N)\,!}{(N\,!)^2}$$

$$N\,! \approx \sqrt{2\pi N}\left(\frac{N}{e}\right)^N$$

Stirling formula for large N values

$$\approx \frac{2^{2N}}{\sqrt{\pi N}} = \frac{e^{2N\ln 2}}{\sqrt{\pi N}}$$

How many determinants in total?

$$N_{\text{det.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}}$$

“Exponential wall”

How many determinants in total?

$$N_{\text{det.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=50}{\approx} 10^{29}$$

How many determinants in total?

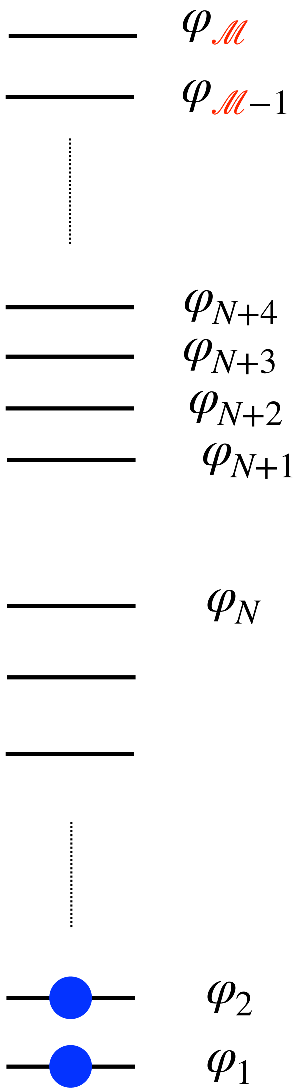
$$N_{\text{det.}} \approx \frac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=400}{\approx} 1.88 \times 10^{239}$$

Truncated CI methods and the size-consistency issue

CI singles and doubles ansatz (CISD):

$$\hat{C} \approx \hat{C}_{\text{CISD}} = C_0 + \sum_{a=N+1}^{\mathscr{M}} \sum_{i=1}^{N} C_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathscr{M}} \sum_{i,j=1}^{N} C_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

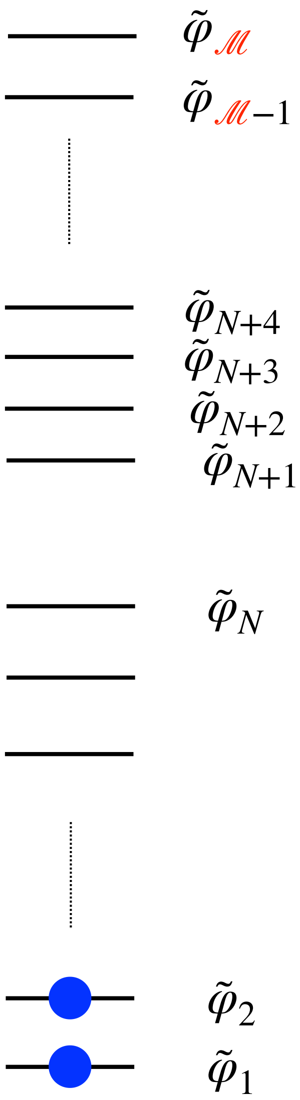
Truncated CI methods and the size-consistency issue



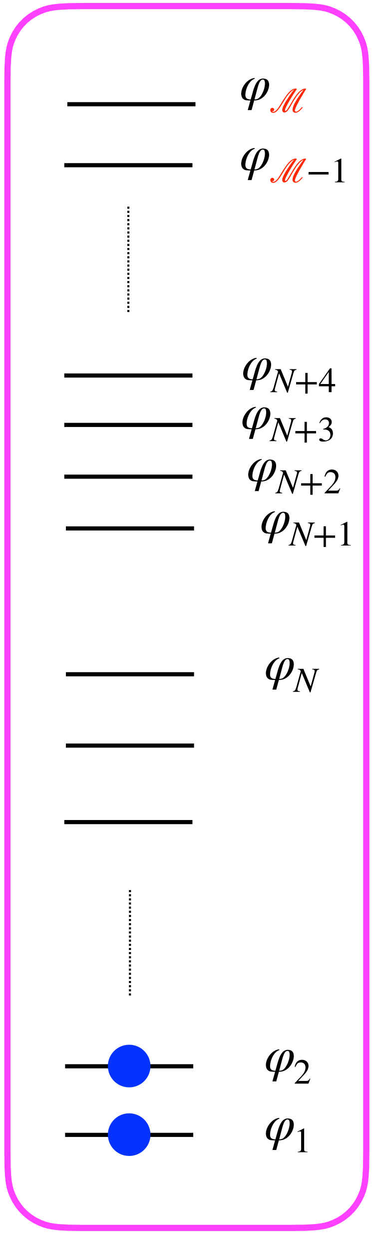
Let us consider two monomers

far apart from each other

(each monomer contains two electrons)



Truncated CI methods and the size-consistency issue

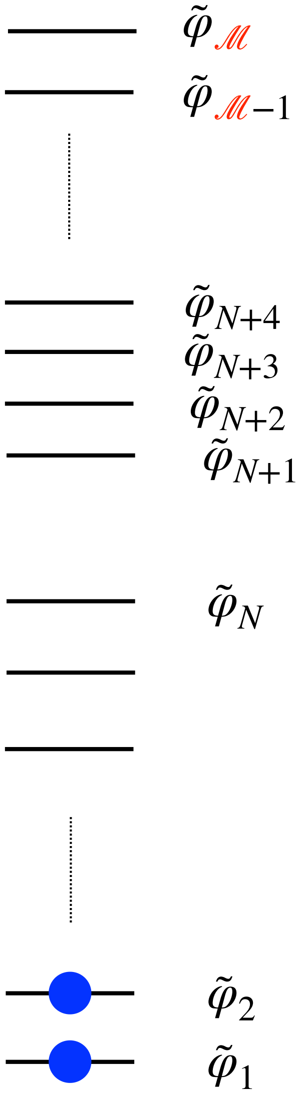


CISD is “exact”

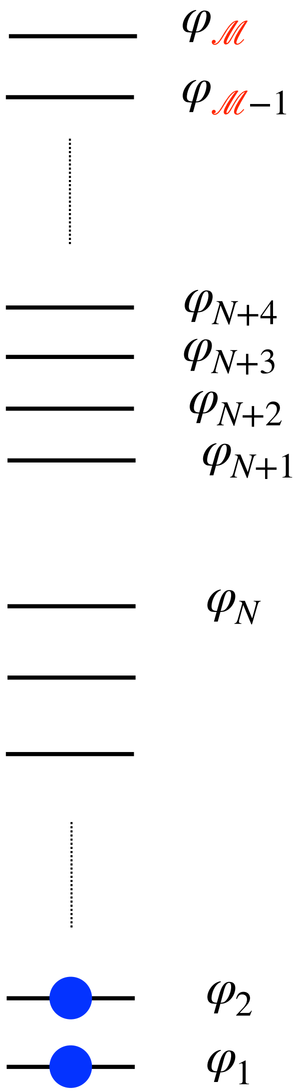
Let us consider two monomers

far apart from each other

(each monomer contains two electrons)



Truncated CI methods and the size-consistency issue



Let us consider two monomers

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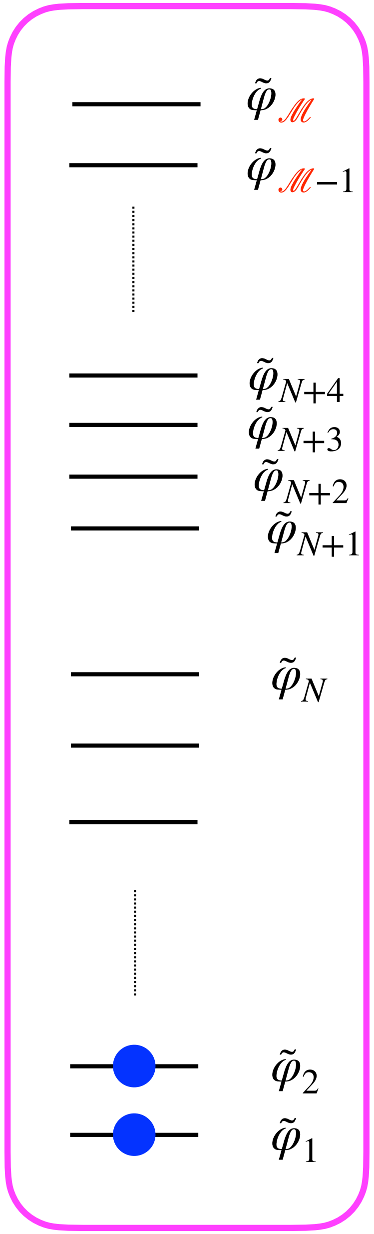


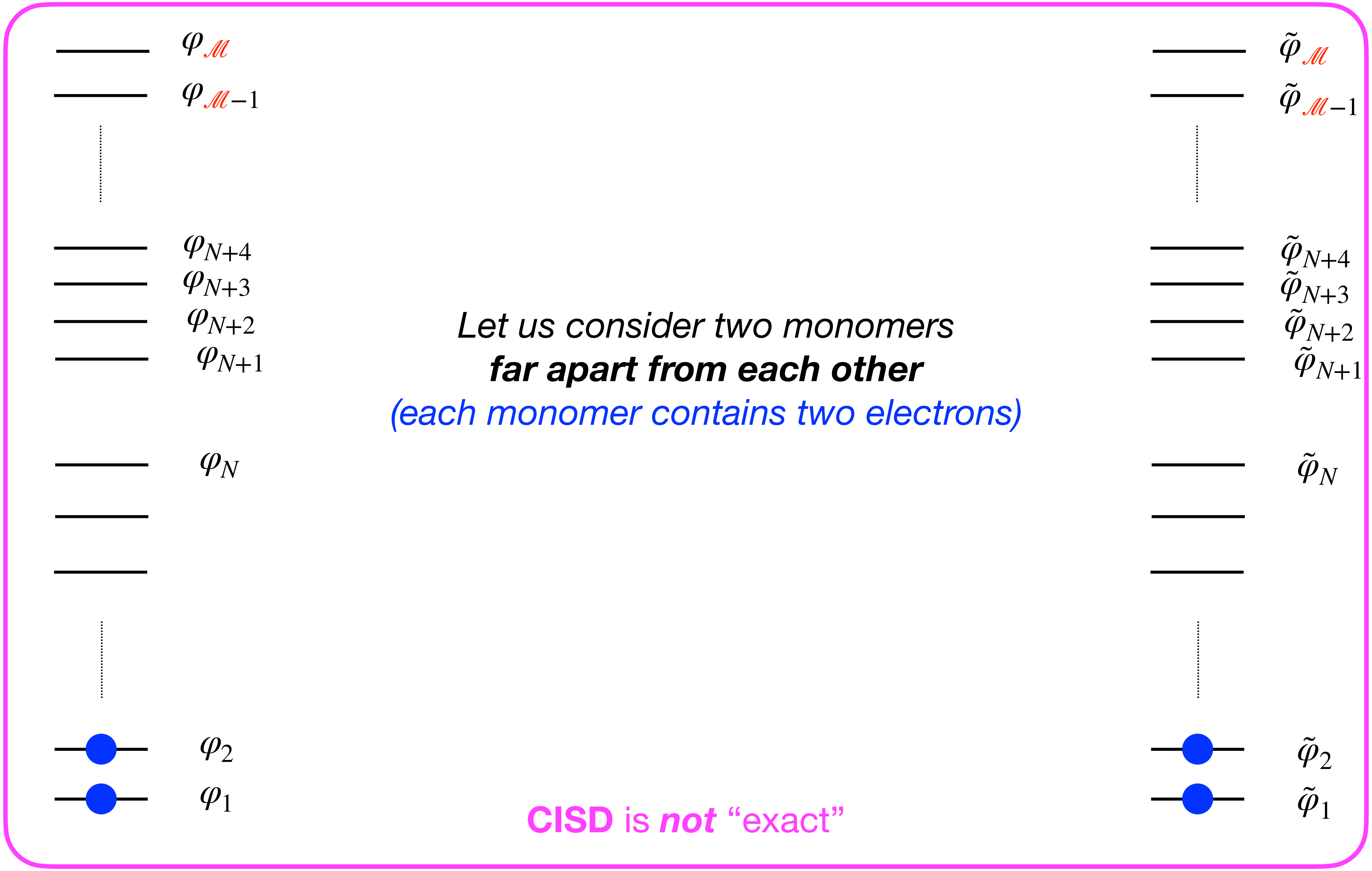
CISD is “exact”

Truncated CI methods and the *size-consistency issue*

Let us consider two monomers
far apart from each other
(each monomer contains two electrons)

CISD is ***not*** “exact”

Truncated CI methods and the size-consistency issue



Let us consider two monomers
far apart from each other
(each monomer contains two electrons)

CISD is ***not*** “exact”

CISD**TQ** would be

Coupled Cluster (CC) theory

$$|\Psi_0\rangle \approx |\Psi(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle$$

$$\hat{T} = t_0 + \sum_{a=N+1}^{\mathcal{M}} \sum_{i=1}^{N} t_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathcal{M}} \sum_{i,j=1}^{N} t_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \sum_{a,b,c=N+1}^{\mathcal{M}} \sum_{i,j,k=1}^{N} t_{ijk}^{abc} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k + \ldots$$

Excitation operator

Coupled Cluster (CC) theory

$$|\Psi_0\rangle \approx |\Psi(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle$$

$$\hat{T} = t_0 + \sum_{a=N+1}^{\mathcal{M}} \sum_{i=1}^{N} t_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathcal{M}} \sum_{i,j=1}^{N} t_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \sum_{a,b,c=N+1}^{\mathcal{M}} \sum_{i,j,k=1}^{N} t_{ijk}^{abc} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k + \ldots$$

To-be-optimized **Coupled Cluster amplitudes**

Coupled Cluster (CC) theory

$$|\Psi_0\rangle \approx |\Psi(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle$$

$$\hat{T} = t_0 + \sum_{a=N+1}^{\mathscr{M}} \sum_{i=1}^{N} t_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathscr{M}} \sum_{i,j=1}^{N} t_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j + \sum_{a,b,c=N+1}^{\mathscr{M}} \sum_{i,j,k=1}^{N} t_{ijk}^{abc} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_i \hat{a}_j \hat{a}_k + \ldots$$

$$e^{\hat{T}} = 1 + \sum_{n=1}^{+\infty} \frac{\hat{T}^n}{n!} = \boxed{\underbrace{\boxed{1+\hat{T}}}_{\text{CI}} + \frac{1}{2}\hat{T}^2 + \frac{1}{6}\hat{T}^3 + \frac{1}{24}\hat{T}^4 + \ldots}$$

CC

Truncated CC theory

$$\hat{T} \rightarrow \hat{T}_{\mathrm{CCSD}} = t_0 + \sum_{a=N+1}^{\mathcal{M}} \sum_{i=1}^{N} t_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathcal{M}} \sum_{i,j=1}^{N} t_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

$$e^{\hat{T}} \rightarrow e^{\hat{T}_{\mathrm{CCSD}}} = 1 + \hat{T}_{\mathrm{CCSD}} + \frac{1}{2} \boxed{\hat{T}_{\mathrm{CCSD}} \hat{T}_{\mathrm{CCSD}}} + \ldots$$

Will generate **triple**
and **quadruple excitations**

Truncated CC theory

$$\hat{T} \rightarrow \hat{T}_{\text{CCSD}} = t_0 + \sum_{a=N+1}^{\mathcal{M}} \sum_{i=1}^{N} t_i^a \, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathcal{M}} \sum_{i,j=1}^{N} t_{ij}^{ab} \, \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i \hat{a}_j$$

$$e^{\hat{T}} \rightarrow e^{\hat{T}_{\text{CCSD}}} = 1 + \hat{T}_{\text{CCSD}} + \frac{1}{2} \boxed{\hat{T}_{\text{CCSD}} \hat{T}_{\text{CCSD}}} + \dots$$

Will generate **triple**
and **quadruple excitations**

**Size-consistency
is restored** ✓

Conventional *(non-variational)* ***optimisation of the CC amplitudes***

$$\hat{H}\left(e^{\hat{T}}|\Phi_0\rangle\right) = E_{\mathrm{CC}}\left(e^{\hat{T}}|\Phi_0\rangle\right)$$

Schrödinger equation for the CC wave function

Conventional *(non-variational)* **optimisation of the CC amplitudes**

$$\begin{tikzcd}
\hat{H}\left(e^{\hat{T}}|\Phi_0\rangle\right) = E_{\mathrm{CC}}\left(e^{\hat{T}}|\Phi_0\rangle\right) \arrow[d, bend right, "e^{-\hat{T}} \times"'] \\
e^{-\hat{T}}\hat{H}\,e^{\hat{T}}|\Phi_0\rangle = E_{\mathrm{CC}}\,e^{-\hat{T}}e^{\hat{T}}|\Phi_0\rangle
\end{tikzcd}$$

Conventional *(non-variational)* ***optimisation of the CC amplitudes***

$$\hat{H}\left(e^{\hat{T}}|\Phi_0\rangle\right) = E_{\text{CC}}\left(e^{\hat{T}}|\Phi_0\rangle\right)$$

$$e^{-\hat{T}}\hat{H}\,e^{\hat{T}}|\Phi_0\rangle = E_{\text{CC}}\,e^{-\hat{T}}e^{\hat{T}}|\Phi_0\rangle$$

$$\hat{\mathscr{H}}_{\text{CC}}(\mathbf{t})|\Phi_0\rangle = E_{\text{CC}}|\Phi_0\rangle$$

$$\boxed{\hat{\mathscr{H}}_{\text{CC}}(\mathbf{t}) = e^{-\hat{T}}\hat{H}\,e^{\hat{T}}}$$

Conventional *(non-variational)* ***optimisation of the CC amplitudes***

$$\hat{\mathscr{H}}_{\mathrm{CC}}(\mathbf{t})\,|\Phi_0\rangle = E_{\mathrm{CC}}\,|\Phi_0\rangle$$

Known!

Effective N-electron
Schrödinger equation

Conventional *(non-variational)* ***optimisation of the CC amplitudes***

$$\boxed{\hat{\mathscr{H}}_{\mathrm{CC}}(\mathbf{t})\,|\,\Phi_0\rangle = E_{\mathrm{CC}}\,|\,\Phi_0\rangle}$$

Effective N-electron
Schrödinger equation

To-be-determined

$$\hat{\mathscr{H}}_{\mathrm{CC}}(\mathbf{t}) = e^{-\hat{T}}\hat{H}\,e^{\hat{T}} = \left(1 - \hat{T} + \frac{1}{2}\hat{T}^2 - \ldots\right)\hat{H}\left(1 + \hat{T} + \frac{1}{2}\hat{T}^2 + \ldots\right)$$

Conventional *(non-variational)* ***optimisation of the CC amplitudes***

$$\boxed{\hat{\mathscr{H}}_{\mathrm{CC}}(\mathbf{t})\,|\Phi_0\rangle = E_{\mathrm{CC}}\,|\Phi_0\rangle}$$

Effective N-electron Schrödinger equation

To-be-determined

$$\hat{\mathscr{H}}_{\mathrm{CC}}(\mathbf{t}) = e^{-\hat{T}}\hat{H}\,e^{\hat{T}} = \underbrace{\left(1-\hat{T}+\frac{1}{2}\hat{T}^2-\ldots\right)\hat{H}\left(1+\hat{T}+\frac{1}{2}\hat{T}^2+\ldots\right)}_{\textit{Expansion } \textbf{\textit{stops exactly}} \textit{ at fourth order in } \hat{T}}$$

Unitary CC (uCC) theory

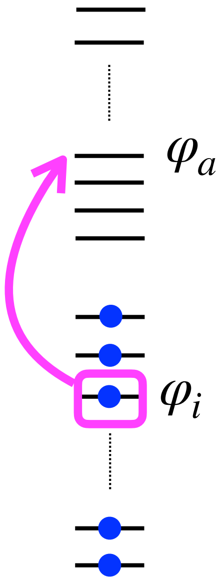
(standard in quantum algorithms for quantum chemistry)

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^\dagger}|\Phi_0\rangle$$

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^\dagger}|\Phi_0\rangle$$

$$\hat{T} = t_0 + \sum_{a=N+1}^{\mathcal{M}}\sum_{i=1}^{N} t_i^a\, \hat{a}_a^\dagger \hat{a}_i + \sum_{a,b=N+1}^{\mathcal{M}}\sum_{i,j=1}^{N} t_{ij}^{ab}\, \hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_i\hat{a}_j + \sum_{a,b,c=N+1}^{\mathcal{M}}\sum_{i,j,k=1}^{N} t_{ijk}^{abc}\, \hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_c^\dagger\hat{a}_i\hat{a}_j\hat{a}_k + \ldots$$

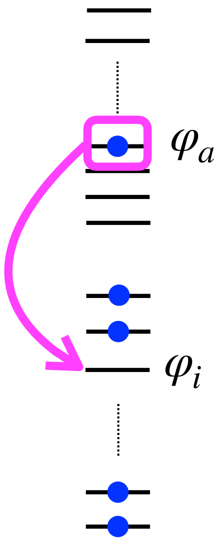


Excitation operator

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^\dagger}|\Phi_0\rangle$$

$$\hat{T}^\dagger = t_0 + \sum_{a=N+1}^{\mathcal{M}}\sum_{i=1}^{N} t_i^a\, \hat{a}_i^\dagger \hat{a}_a + \sum_{a,b=N+1}^{\mathcal{M}}\sum_{i,j=1}^{N} t_{ij}^{ab}\, \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_b \hat{a}_a + \sum_{a,b,c=N+1}^{\mathcal{M}}\sum_{i,j,k=1}^{N} t_{ijk}^{abc}\, \hat{a}_k^\dagger \hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_c \hat{a}_b \hat{a}_a + \ldots$$



De-excitation operator

*with the **same** CC amplitudes*

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = \underbrace{e^{\hat{T}-\hat{T}^\dagger}}_{\textbf{Unitary transformation}}|\Phi_0\rangle$$

$$\boxed{\langle\Psi_{\mathrm{uCC}}(\mathbf{t})|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = \langle\Phi_0|\Phi_0\rangle}$$

*The square norm is **preserved!***

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = \underbrace{e^{\hat{T}-\hat{T}^{\dagger}}}_{\text{Unitary transformation}}|\Phi_0\rangle$$

$$\boxed{\langle\Psi_{\mathrm{uCC}}(\mathbf{t})|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = 1}$$

The square norm is preserved!

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^{\dagger}}|\Phi_0\rangle$$

Variational evaluation of the energy:

$$E_{\mathrm{uCC}} = \min_{\mathbf{t}} \left\{ \frac{\langle \Psi_{\mathrm{uCC}}(\mathbf{t})|\hat{H}|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle}{\langle \Psi_{\mathrm{uCC}}(\mathbf{t})|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle} \right\}$$

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^\dagger}|\Phi_0\rangle$$

Variational evaluation of the energy:

$$E_{\mathrm{uCC}} = \min_{\mathbf{t}} \left\{ \frac{\langle\Psi_{\mathrm{uCC}}(\mathbf{t})|\hat{H}|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle}{\langle\Psi_{\mathrm{uCC}}(\mathbf{t})|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle} \right\}$$

$$= \min_{\mathbf{t}} \left\{ \langle\Psi_{\mathrm{uCC}}(\mathbf{t})|\hat{H}|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle \right\}$$

Unitary CC (uCC) theory

$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^{\dagger}}|\Phi_0\rangle$$

Variational evaluation of the energy:

$$\boxed{\hat{\mathscr{H}}_{\mathrm{uCC}}(\mathbf{t}) = e^{-\left(\hat{T}-\hat{T}^{\dagger}\right)}\hat{H}\,e^{\left(\hat{T}-\hat{T}^{\dagger}\right)} \neq e^{-\hat{T}}\hat{H}\,e^{\hat{T}} = \hat{\mathscr{H}}_{\mathrm{CC}}(\mathbf{t})}$$

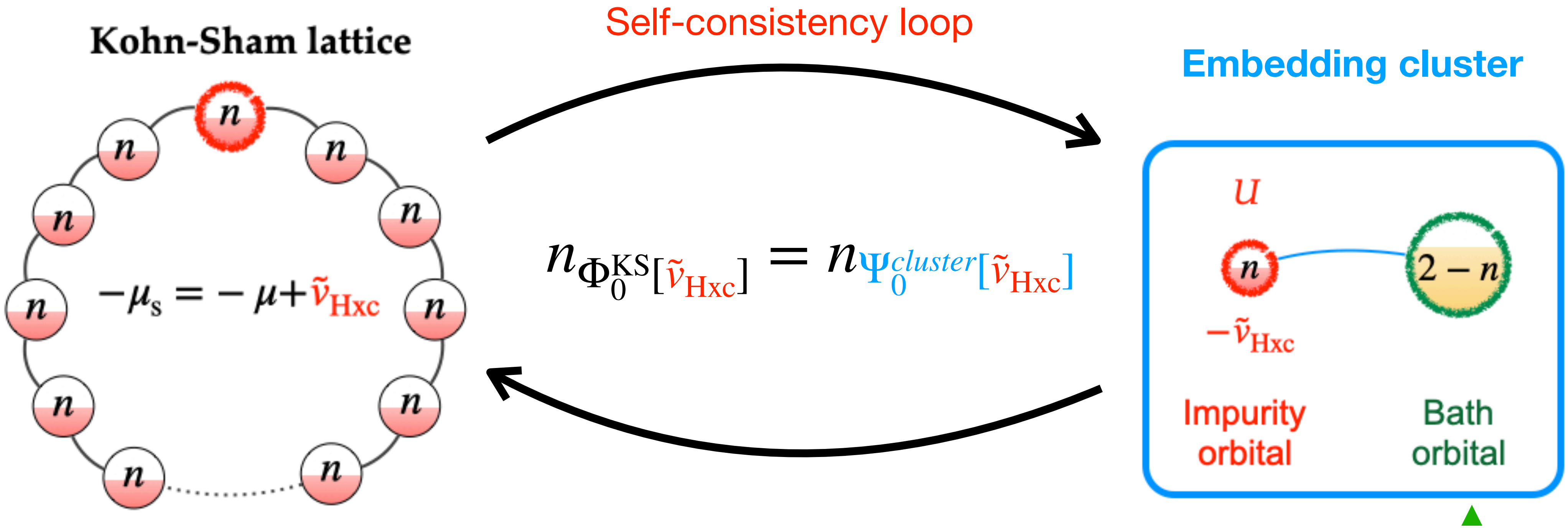
$$E_{\mathrm{uCC}} = \min_{\mathbf{t}}\left\{\langle\Phi_0|\hat{\mathscr{H}}_{\mathrm{uCC}}(\mathbf{t})|\Phi_0\rangle\right\}$$

Quantum embedding theory

$$n, \Psi$$

Local potential-functional embedding theory (LPFET)

inspired by Density Matrix Embedding Theory (DMET)



$$n_{\Phi_0^{\rm KS}[\tilde{v}_{\rm Hxc}]} = n_{\Psi_0^{cluster}[\tilde{v}_{\rm Hxc}]}$$

$$\gamma^{\rm KS}(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \varphi_i(\mathbf{r})\varphi_i(\mathbf{r}')$$

Kohn-Sham one-electron
reduced **density matrix**

S. Sekaran, M. Saubanère, and E. Fromager, Computation ***2022****, 10, 45.*
S. Sekaran, M. Tsuchiizu, M. Saubanère, and E. Fromager, Phys. Rev. B ***104****, 035121 (2021).*
U. Mordovina, T. E. Reinhard, I. Theophilou, H. Appel, and A. Rubio, J. Chem. Theory Comput. ***15****, 5209 (2019).*
W. Bulik, G. E. Scuseria, and J. Dukelsky, Phys. Rev. B ***89****, 035140 (2014).*
G. Knizia and G. K.-L. Chan, Phys. Rev. Lett. ***109****, 186404 (2012).*