An introduction to ab initio Quantum Chemistry:

Mean field approximation and electron correlation

Emmanuel Fromager

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

Ab initio *molecular electronic structure theory*

Electronic Schrödinger equation

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

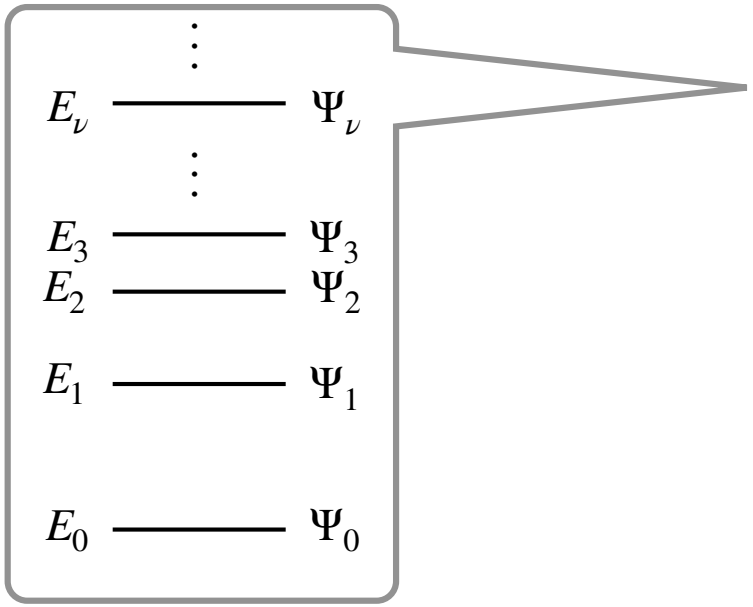
Electronic Schrödinger equation

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

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

Electronic Schrödinger equation

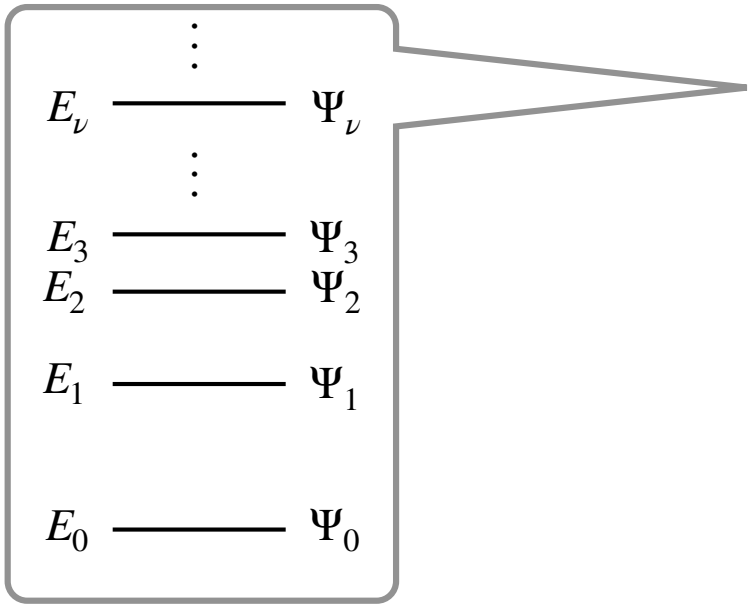
$$\hat{H}\,|\Psi_I\rangle = E_I\,|\Psi_I\rangle$$



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

Electronic Schrödinger equation

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



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

unknown!

Electronic Schrödinger equation

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

Corresponding *electronic wave function*

unknown!

Electronic Schrödinger equation

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

Corresponding *electronic wave function*

$$\Psi_I \equiv \Psi_I(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_N)$$

Electronic coordinates

Electronic Schrödinger equation

Space coordinates of electron i

Spin coordinate of electron i (up or down)

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

$$\Psi_I \equiv \Psi_I(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \ldots, \mathbf{x}_i, \ldots, \mathbf{x}_N)$$

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

known!

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

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

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

"first quantization" representation

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

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

Kinetic energy
of the ith electron

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

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

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

ith electron - nuclei
attraction energy

Electronic Schrödinger equation

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ith electron - nuclei
attraction energy

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

Electronic Schrödinger equation

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

Nuclei are fixed
(Born-Oppenheimer approximation)

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

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

ith electron - nuclei
attraction energy

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

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

ith electron - nuclei
attraction energy

ith electron - jth electron
repulsion energy

Electronic Schrödinger equation

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

Electronic Hamiltonian
operator

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

No parameters!

Electronic Schrödinger equation

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No parameters! ***Ab initio*** *quantum chemistry****!***

Electronic Schrödinger equation

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

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

The electronic problem is solved
for a **fixed** molecular geometry R

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

Born-Oppenheimer approximation

The electronic problem is solved for a **fixed** molecular geometry R

$$\hat{H} \equiv \hat{H}(R)$$

Electronic Schrödinger equation

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

Born-Oppenheimer approximation

The electronic problem is solved for a **fixed** molecular geometry R

$$\hat{H} \equiv \hat{H}(R) \longrightarrow E_I \equiv E_I(R)$$

Electronic Schrödinger equation

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

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

Born-Oppenheimer approximation

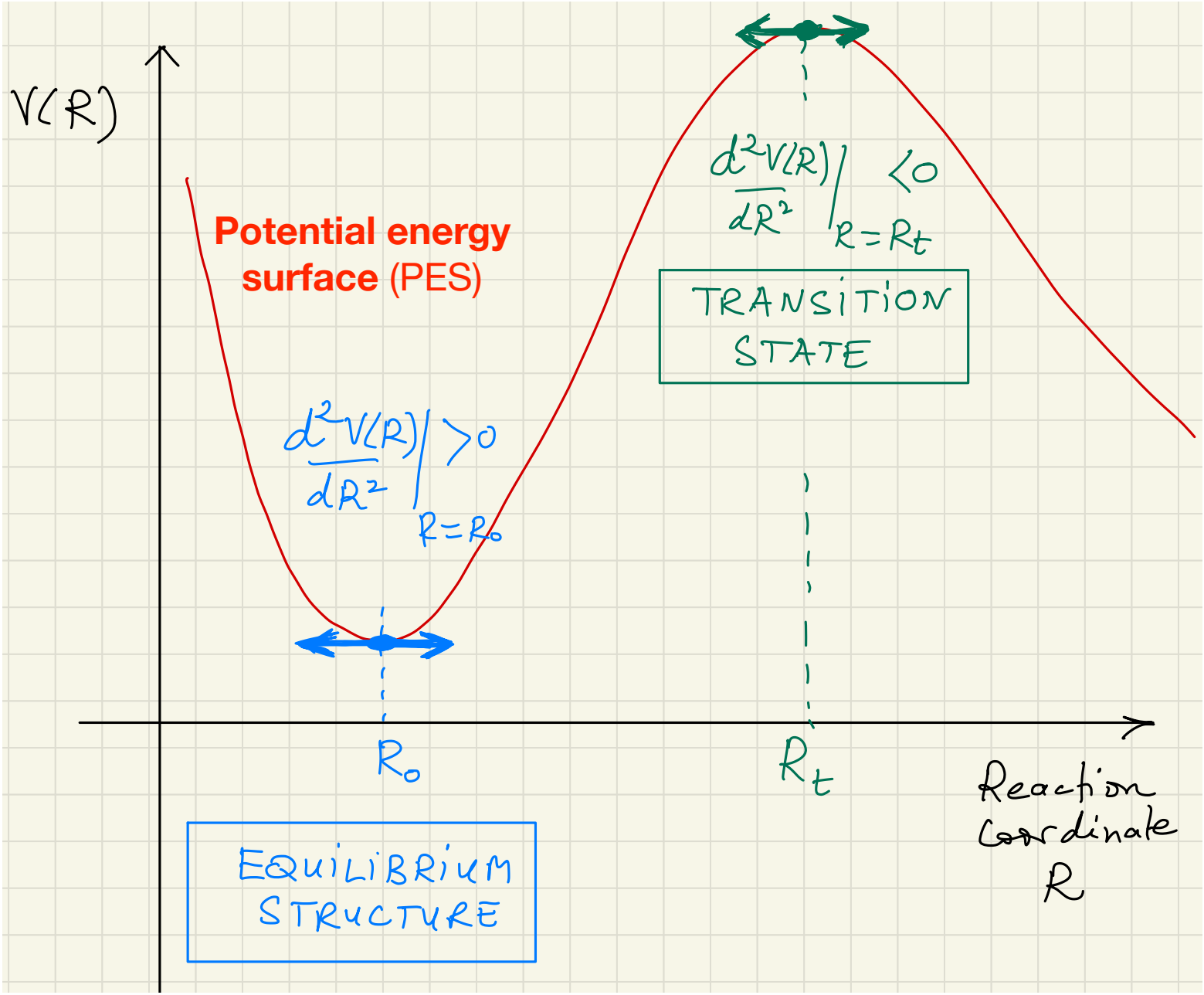
The electronic problem is solved for a **fixed** molecular geometry R

$$E_I \equiv E_I(R)$$

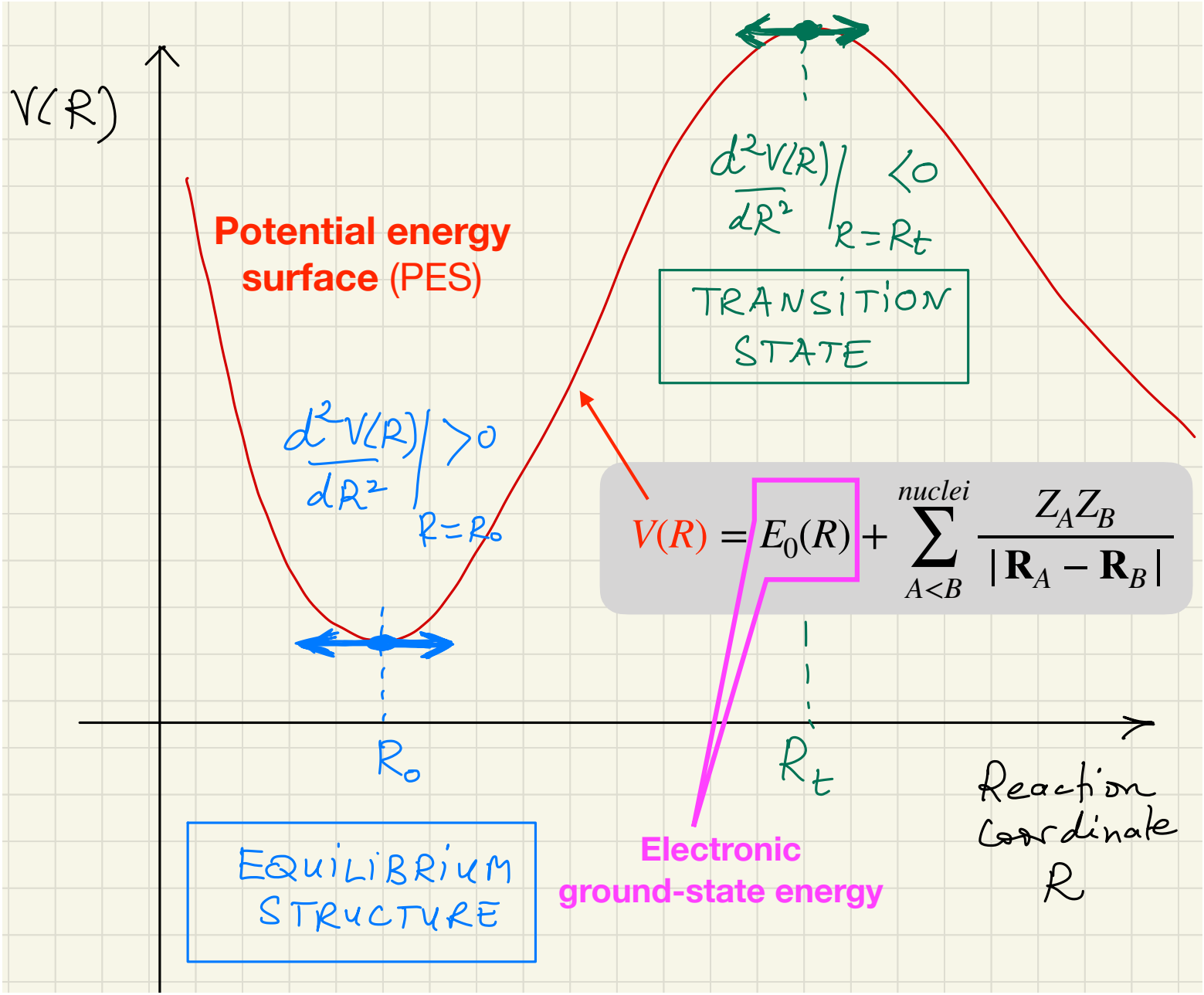
Potential energy surfaces

Why solving the electronic Schrödinger equation?

Computation of chemical reaction paths



Computation of reaction paths in the ground electronic state



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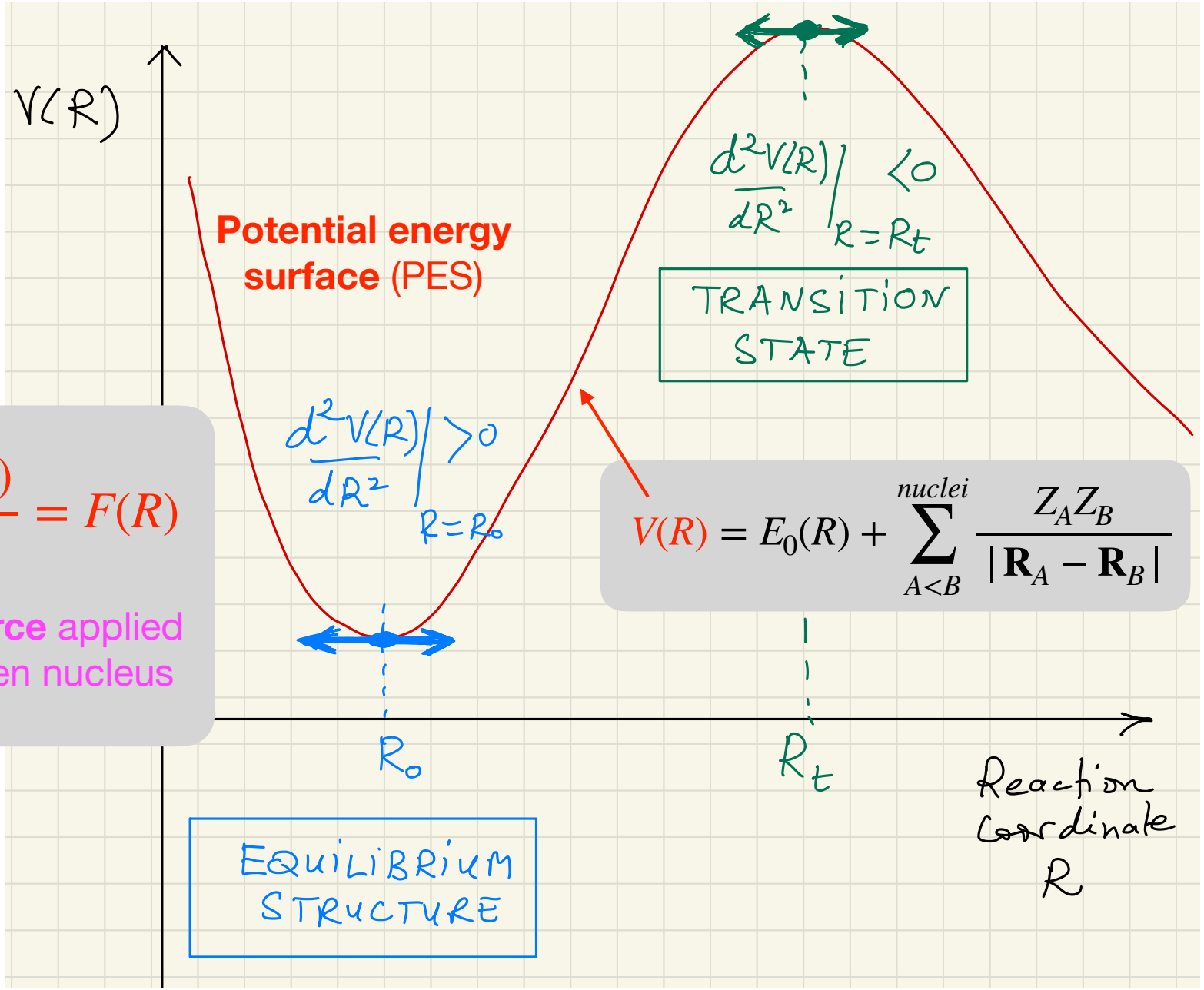

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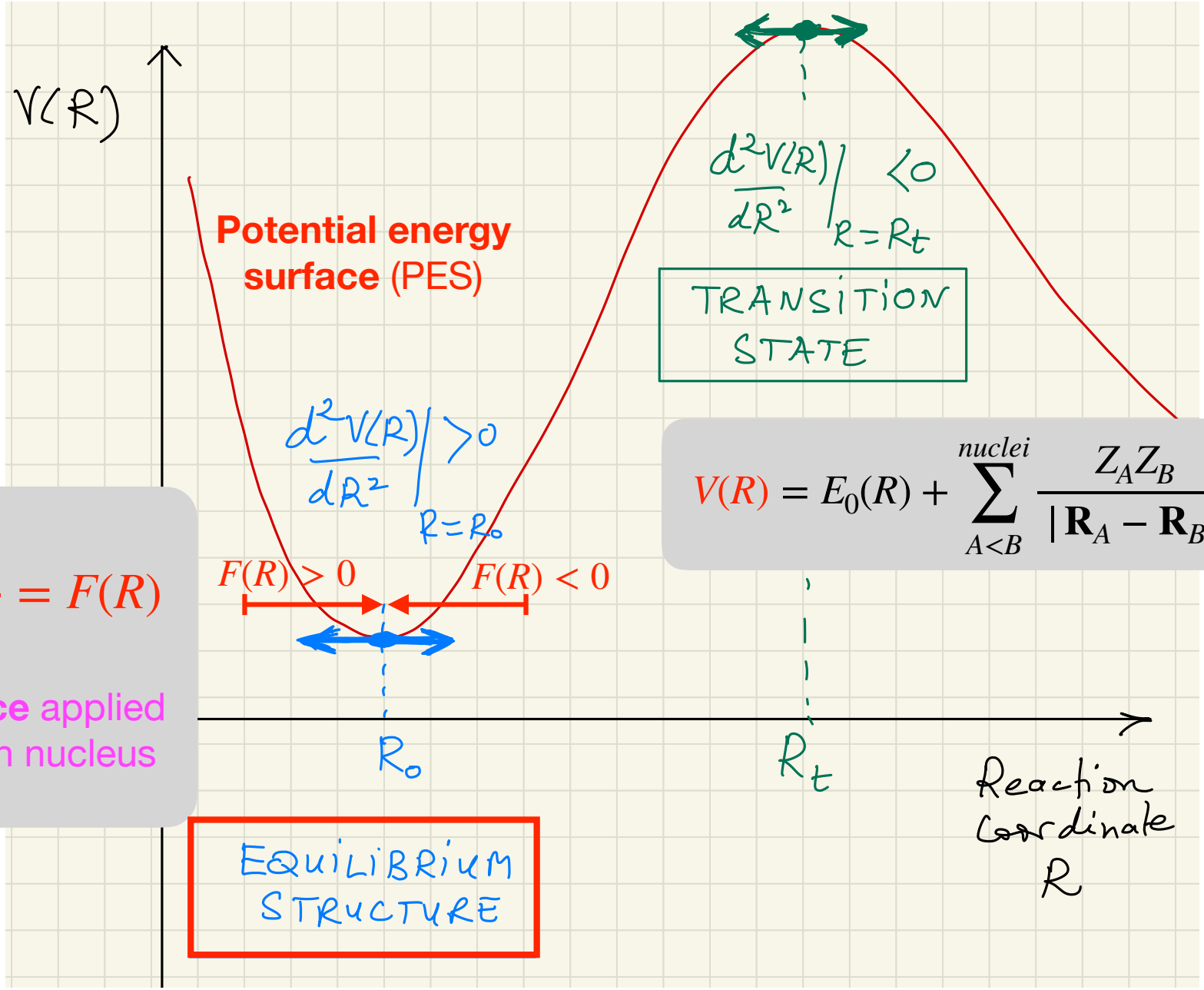
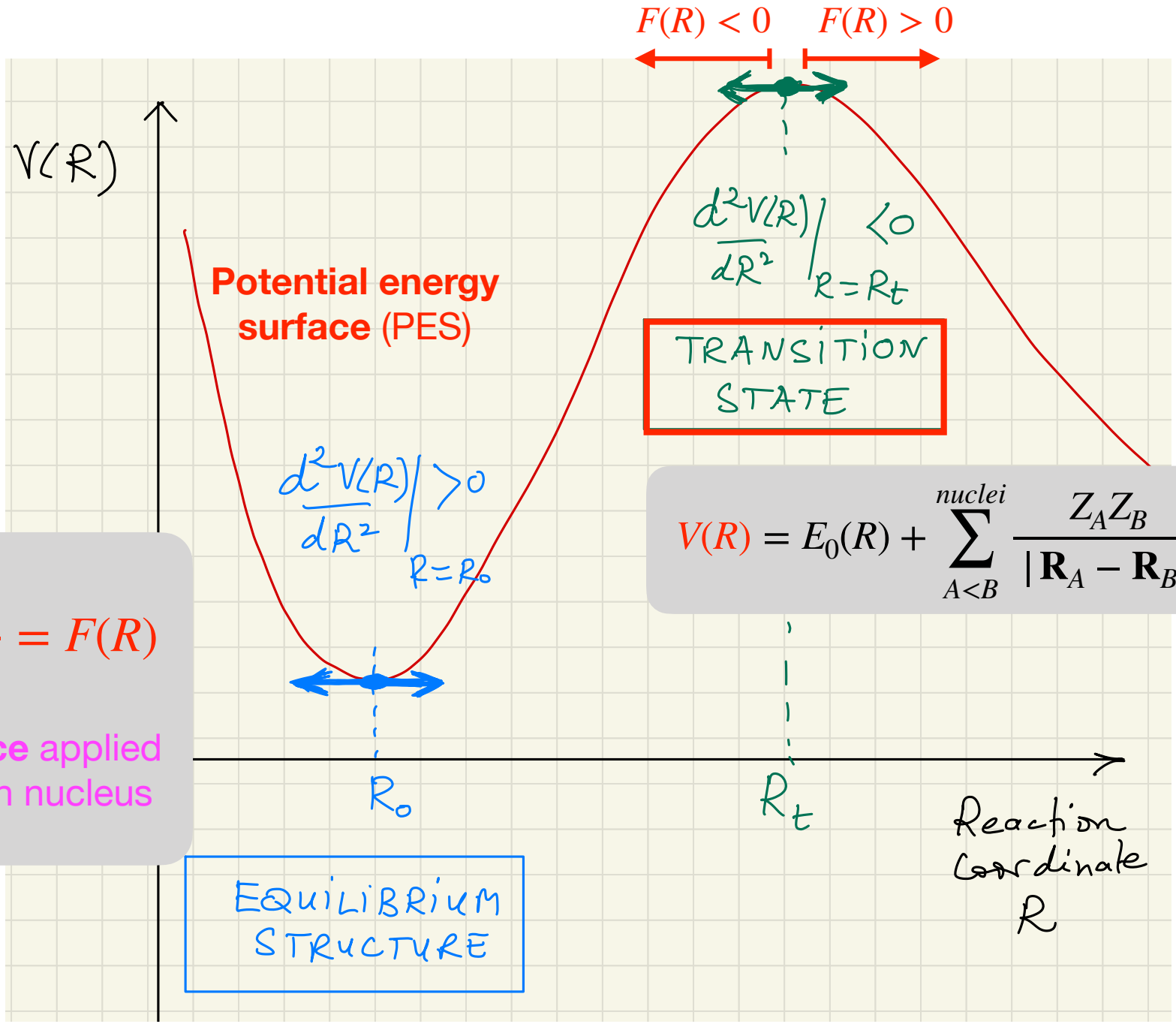


$$-\frac{dV(R)}{dR} = F(R)$$

Total force applied to a given nucleus

$$V(R) = E_0(R) + \sum_{A<B}^{nuclei} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}$$

Computation of reaction paths in the ground electronic state



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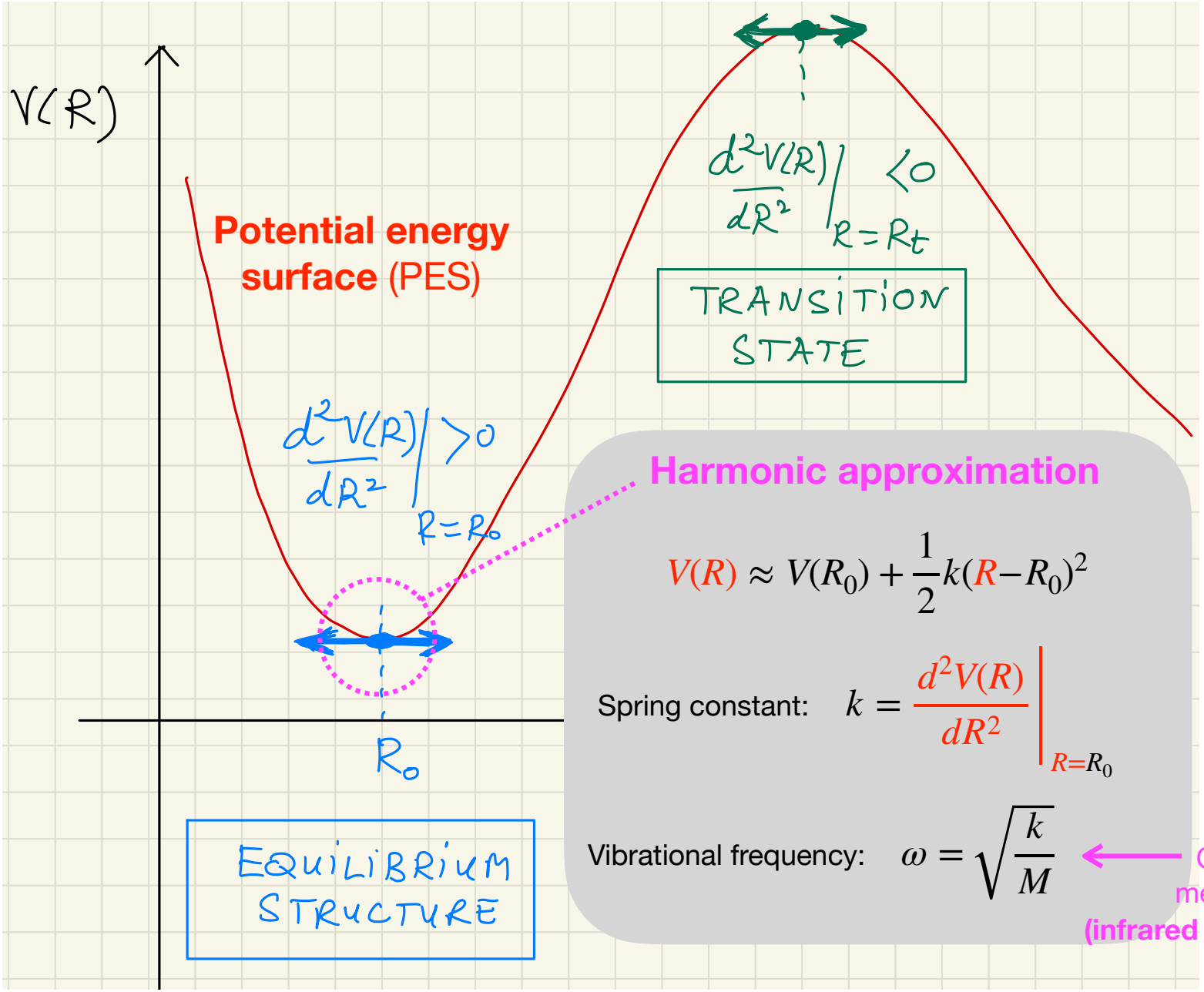
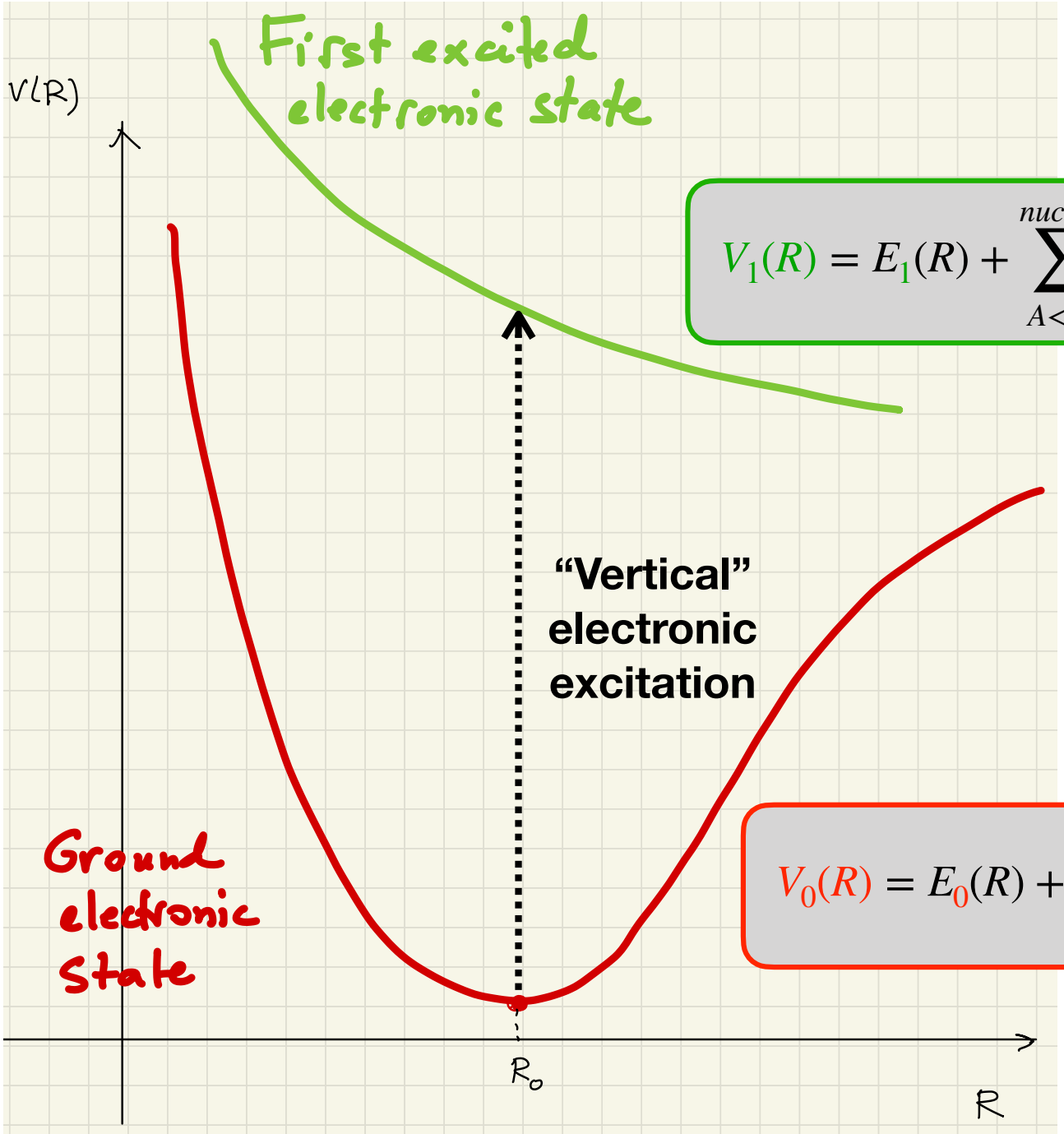
Vibrational molecular spectroscopy



UV-visible electronic spectroscopy



Electronic Schrödinger equation

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

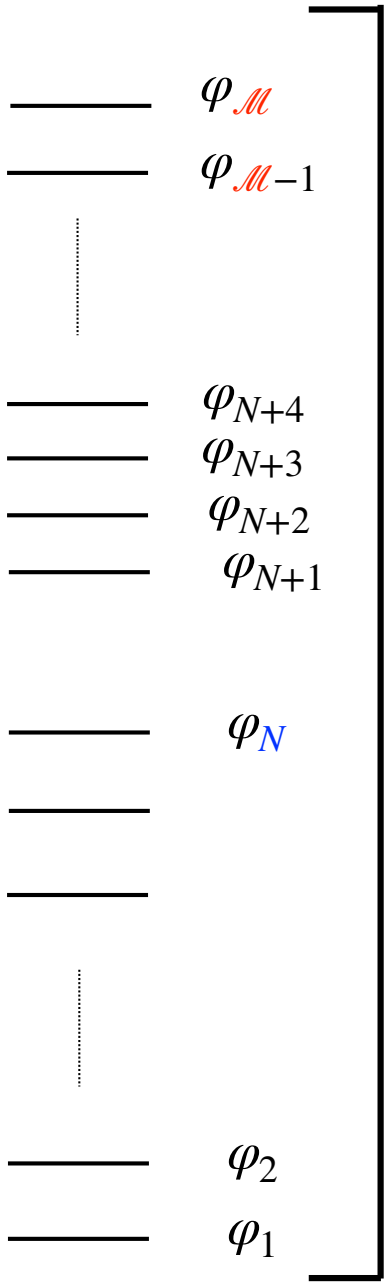
$$\Downarrow$$

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

Corresponding *electronic quantum states*

Encoding *of many-electron quantum states*
(in second quantization)

From the one-electron to the many-electron problem



spin (↑ or ↓)

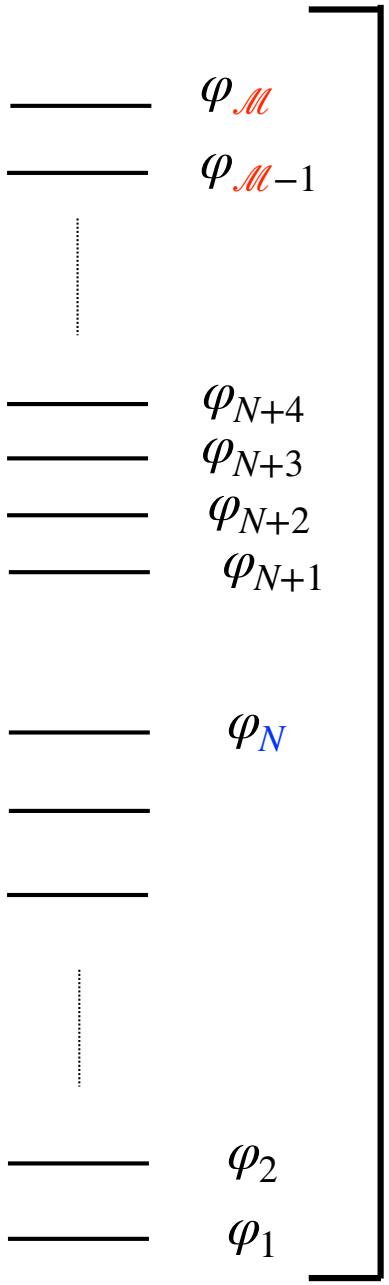
$$\varphi_i(\mathbf{x}) \equiv \varphi_i(\mathbf{r}, \sigma) \equiv \varphi_i(x, y, z, \sigma)$$

space coordinates

Molecular (spin) orbitals

(One-electron wave functions)

From the one-electron to the many-electron problem



Molecular spin orbitals (MOs)

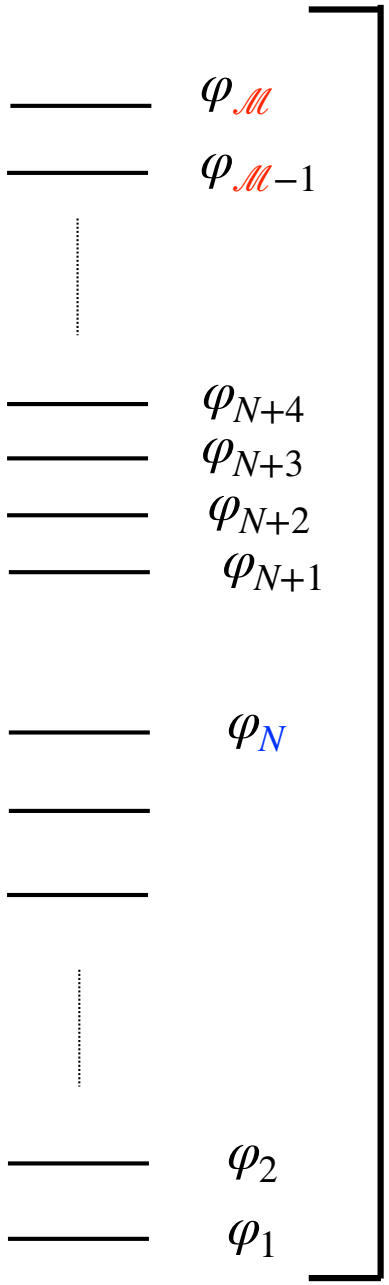
$$\varphi_i(\mathbf{x}) \equiv \varphi_i(\mathbf{r},\sigma) \equiv \varphi_i(x,y,z,\sigma)$$

Atomic (spin) orbitals

$$\chi_\mu(\mathbf{x}) \sim \chi(\mathbf{r}-\mathbf{R}_A)$$ ← Centered on nucleus A

$$\chi(\mathbf{r}) = \chi(x,y,z) \sim x^n y^m z^p\, e^{-\alpha\left(x^2+y^2+z^2\right)}$$

From the one-electron to the many-electron problem



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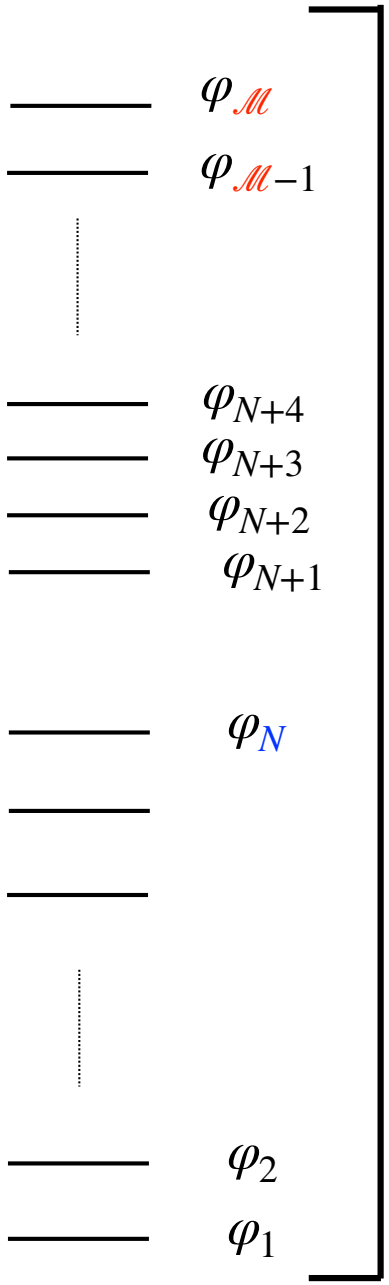
$n = m = p = 0 \rightarrow$ "s orbital"

$n = 1,\ m = p = 0 \rightarrow$ "p_x orbital"

$n = 0,\ m = 1,\ p = 0 \rightarrow$ "p_y orbital"

$n = 0 = m,\ p = 1 \rightarrow$ "p_z orbital"

From the one-electron to the many-electron problem



Molecular spin orbitals (MOs)

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$$\varphi_i(\mathbf{x}) = \sum_{\mu=1}^{\mathcal{M}} C_{\mu i}\,\chi_\mu(\mathbf{x})$$

Atomic (spin) orbitals

$$\chi_\mu(\mathbf{x}) \sim \chi(\mathbf{r}-\mathbf{R}_A)$$ ← Centered on nucleus A

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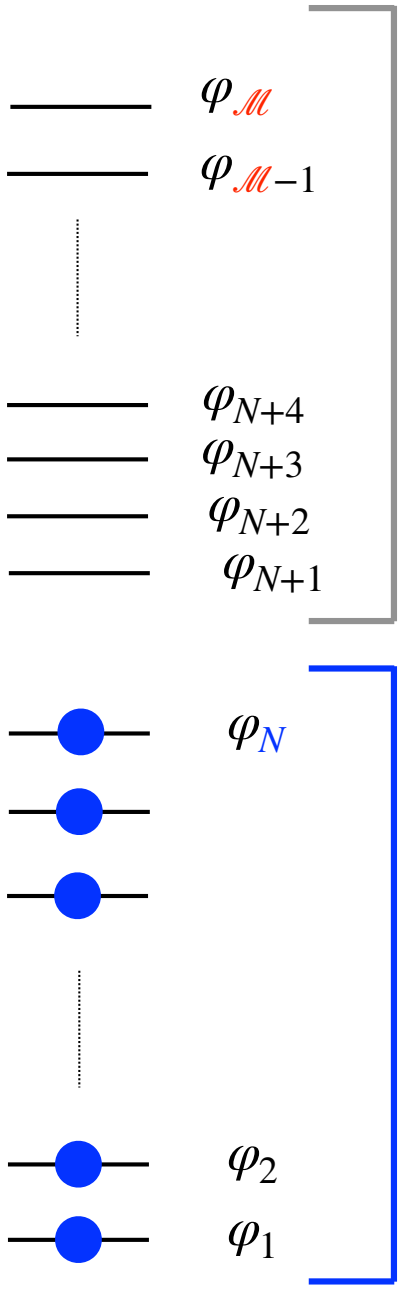
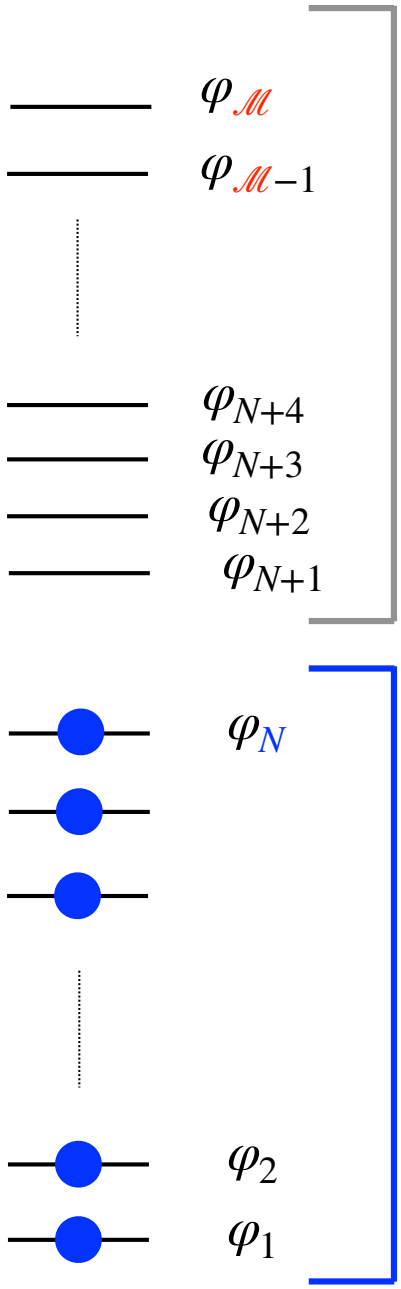
From the one-electron to the many-electron problem



Unoccupied orbitals (virtuals)

Single electronic configuration

From the one-electron to the many-electron problem

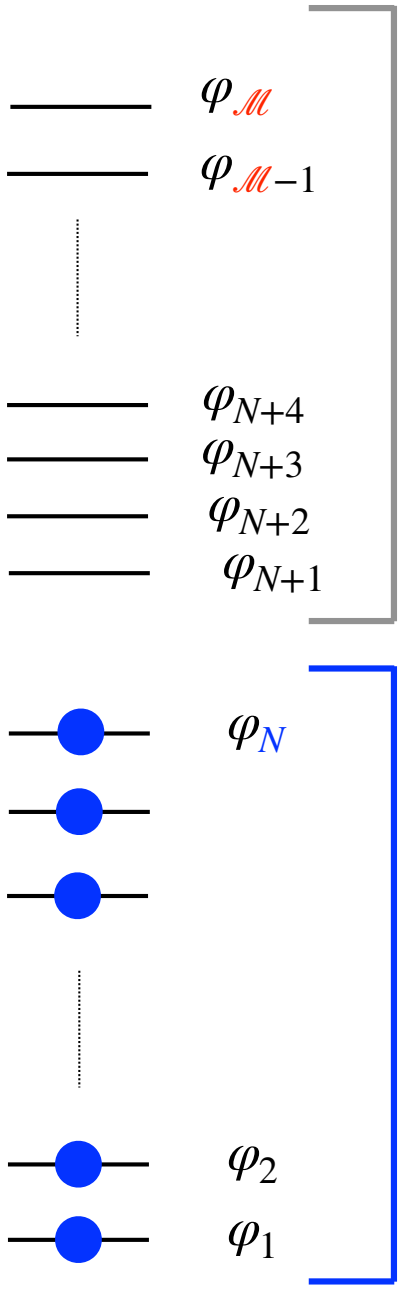


Unoccupied orbitals

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

"second quantization" representation

From the one-electron to the many-electron problem



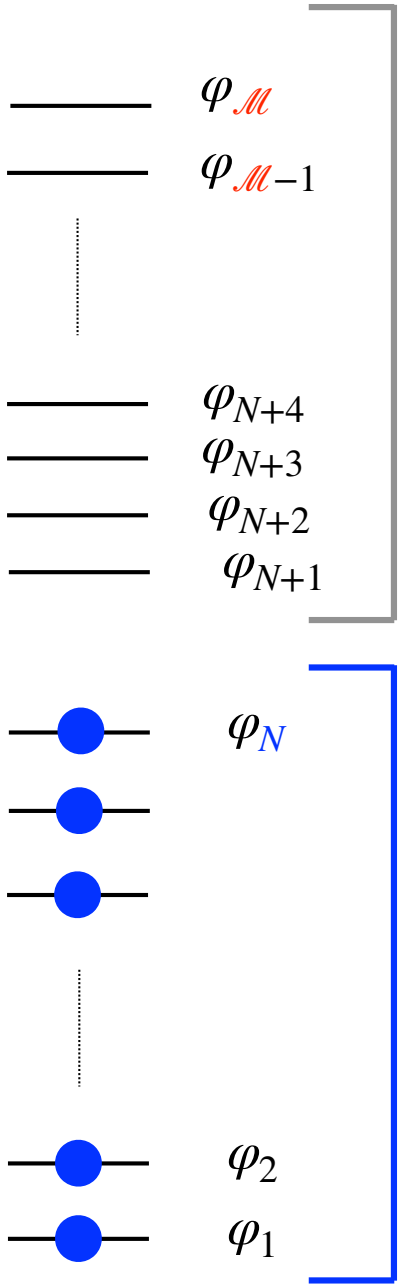
Unoccupied orbitals

Creation operators

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

"second quantization" representation

From the one-electron to the many-electron problem



Unoccupied orbitals

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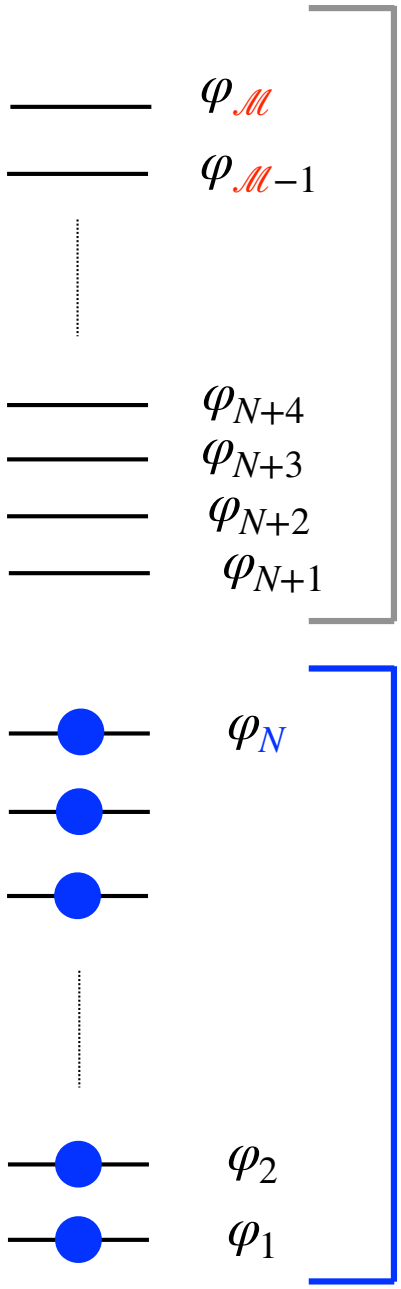
From the one-electron to the many-electron problem

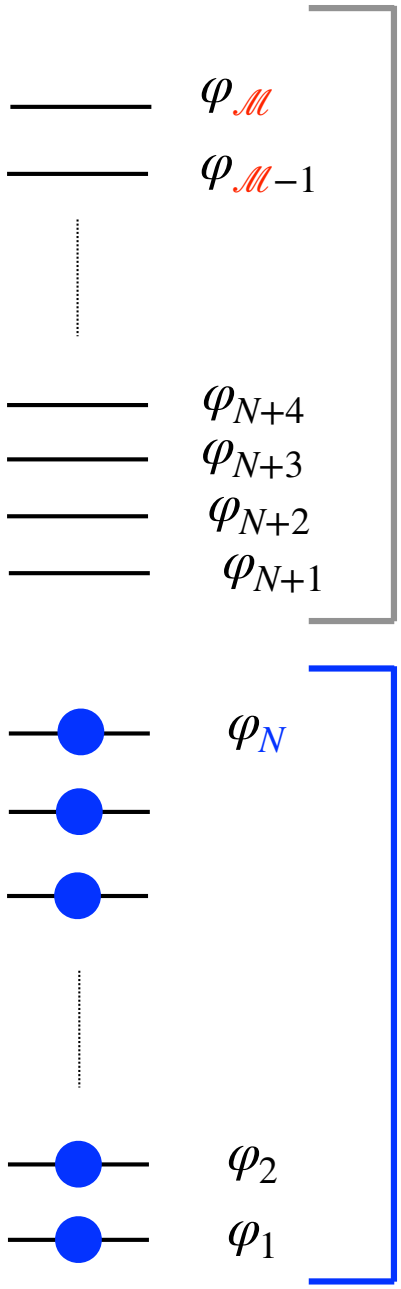


Unoccupied orbitals

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

Slater determinant

From the one-electron to the many-electron problem



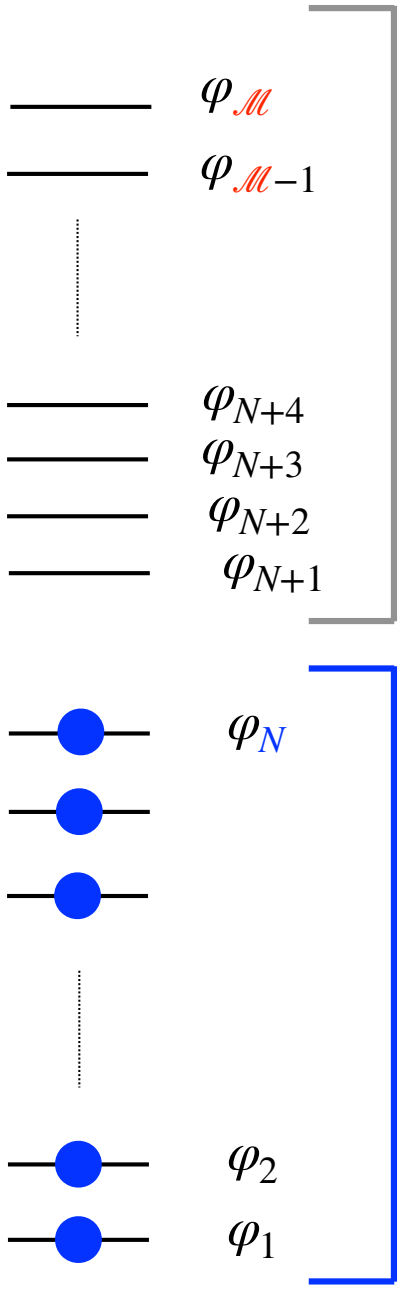
Unoccupied orbitals

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

$$\equiv |1_1 1_2 \ldots 1_N 0_{N+1} \ldots 0_{\mathscr{M}}\rangle$$

Spin orbital occupation encoding!

From the one-electron to the many-electron problem



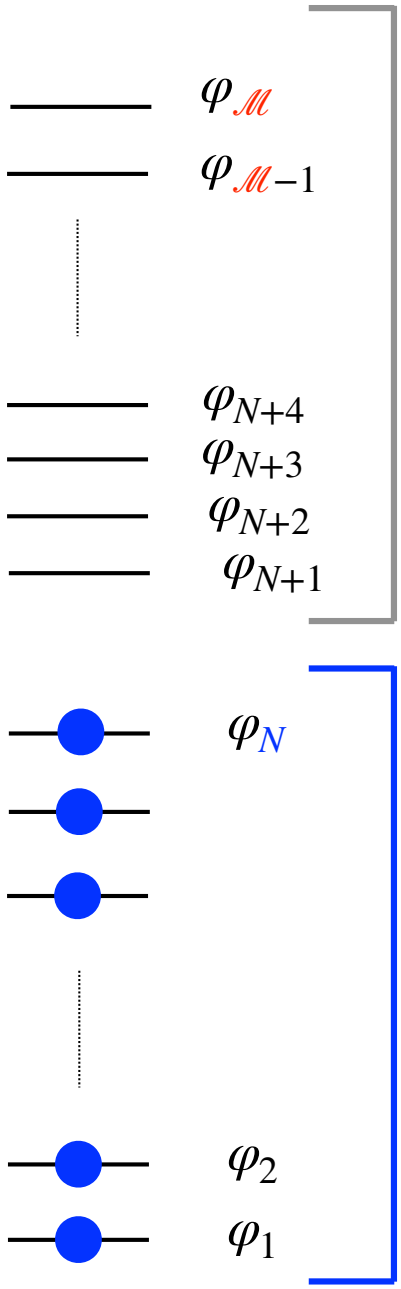
Unoccupied orbitals

$$|\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\mathrm{vac}\rangle \approx |\Psi_0\rangle$$

Slater determinant

"Mean-field approximation"

From the one-electron to the many-electron problem



Unoccupied orbitals

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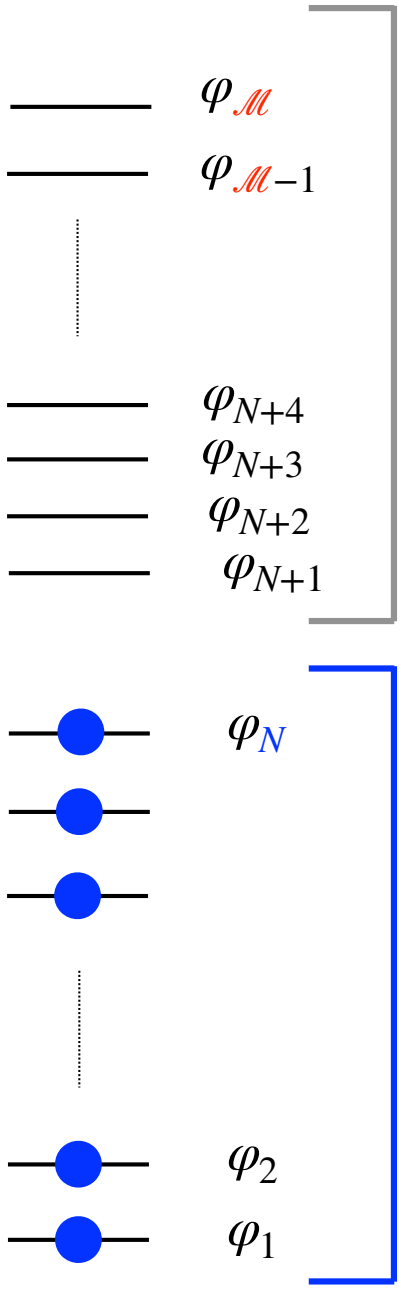
Slater determinant

Hartree-Fock approximation $\Leftrightarrow$ "Mean-field approximation"

From the one-electron to the many-electron problem



Unoccupied orbitals

Single electronic configuration:
no electron correlation (by definition)

$$|\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\mathrm{vac}\rangle \approx |\Psi_0\rangle$$

Slater determinant

Hartree-Fock approximation $\Leftrightarrow$ "Mean-field approximation"

Description of electron correlation

(through a multi-determinant wave function)

$$|\Psi_0\rangle \approx \underbrace{|\Phi_0\rangle}_{\text{Reference determinant}} + \sum_{I>0} C_I \underbrace{|\Phi_I\rangle}_{\text{“Excited” determinants}}$$

If *all* determinants are taken into account (“exact” solution):

Full Configuration Interaction (FCI) method ⇔ “exact diagonalization”

Description of electron correlation

(through a multi-determinant wave function)

$$|\Psi_0\rangle \approx \underbrace{|\Phi_0\rangle}_{\text{Reference determinant}} + \sum_{I>0} C_I \underbrace{|\Phi_I\rangle}_{\text{“Excited” determinants}}$$

???

If *all* determinants are taken into account (“exact” solution):

Full Configuration Interaction (FCI) method ⇔ “exact diagonalization”

Some important theorems *(for quantum chemists)*

Ground-state electronic Schrödinger equation

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

Lowest many-electron energy

Rayleigh-Ritz variational principle

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

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

Expectation value of the energy

Rayleigh-Ritz variational principle

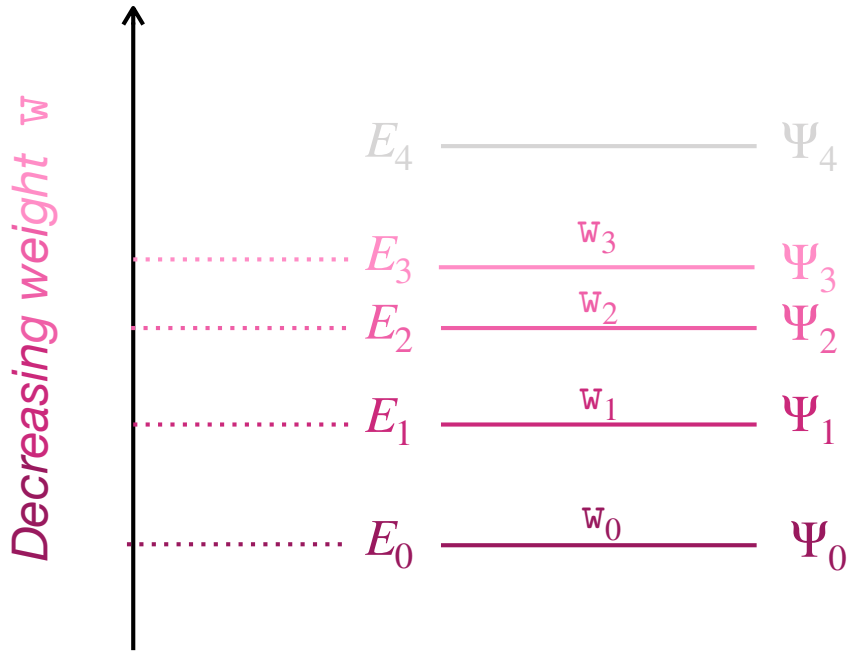
Theorem: For any *trial* wave function Ψ, we have

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

Expectation value of the energy

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

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

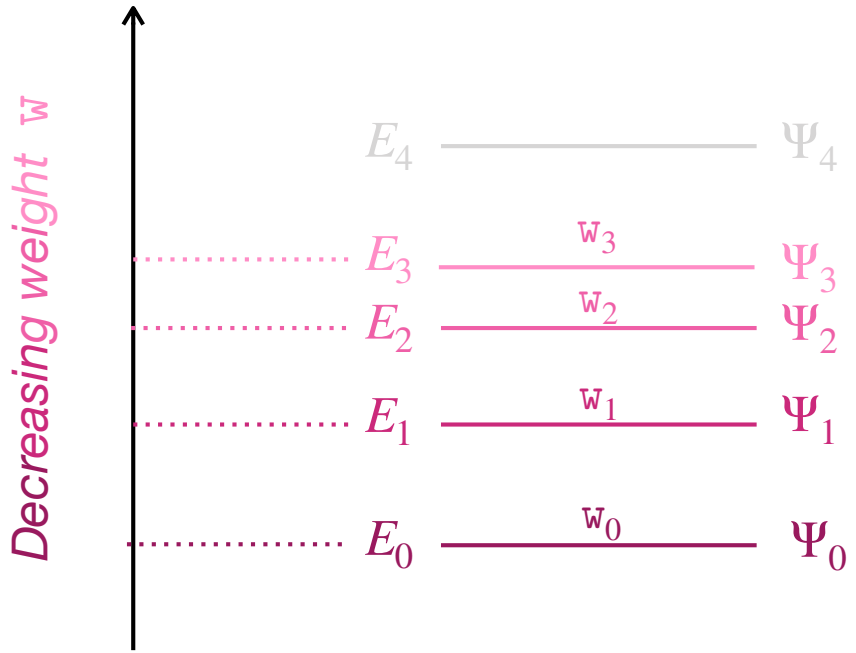


Theorem 2:

$$w_0 \frac{\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle} + w_1 \frac{\langle \tilde{\Psi}_1 | \hat{H} | \tilde{\Psi}_1 \rangle}{\langle \tilde{\Psi}_1 | \tilde{\Psi}_1 \rangle} + \ldots + w_M \frac{\langle \tilde{\Psi}_M | \hat{H} | \tilde{\Psi}_M \rangle}{\langle \tilde{\Psi}_M | \tilde{\Psi}_M \rangle} \geq w_0 E_0 + w_1 E_1 + \ldots + w_M E_M$$

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).*

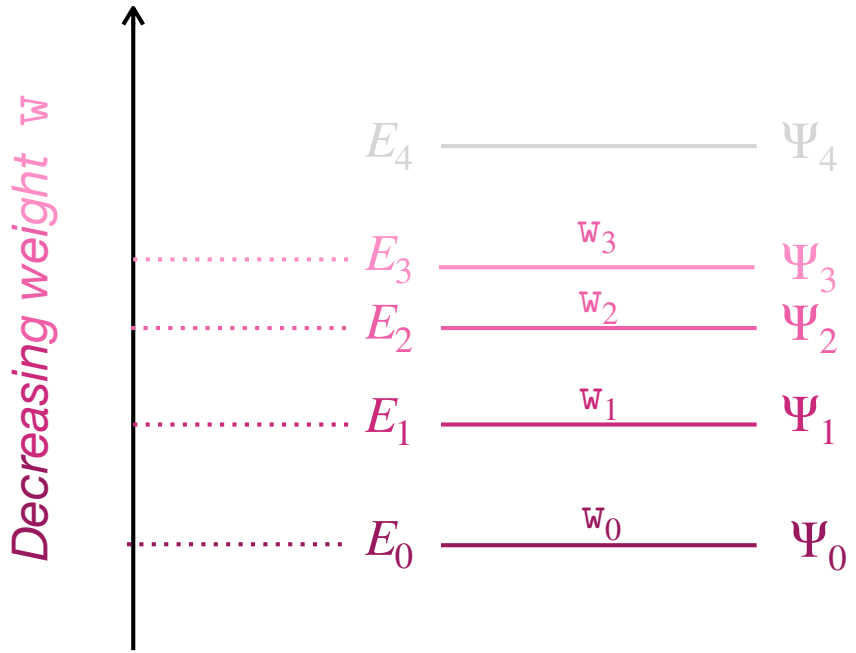
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$w_0 \frac{\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle} + w_1 \frac{\langle \tilde{\Psi}_1 | \hat{H} | \tilde{\Psi}_1 \rangle}{\langle \tilde{\Psi}_1 | \tilde{\Psi}_1 \rangle} + \ldots + w_M \frac{\langle \tilde{\Psi}_M | \hat{H} | \tilde{\Psi}_M \rangle}{\langle \tilde{\Psi}_M | \tilde{\Psi}_M \rangle} \geq w_0 E_0 + w_1 E_1 + \ldots + w_M E_M$$

Arbitrary **ordered positive weights** $\leftarrow$ $w_0 \geq w_1 \geq \ldots \geq w_M$

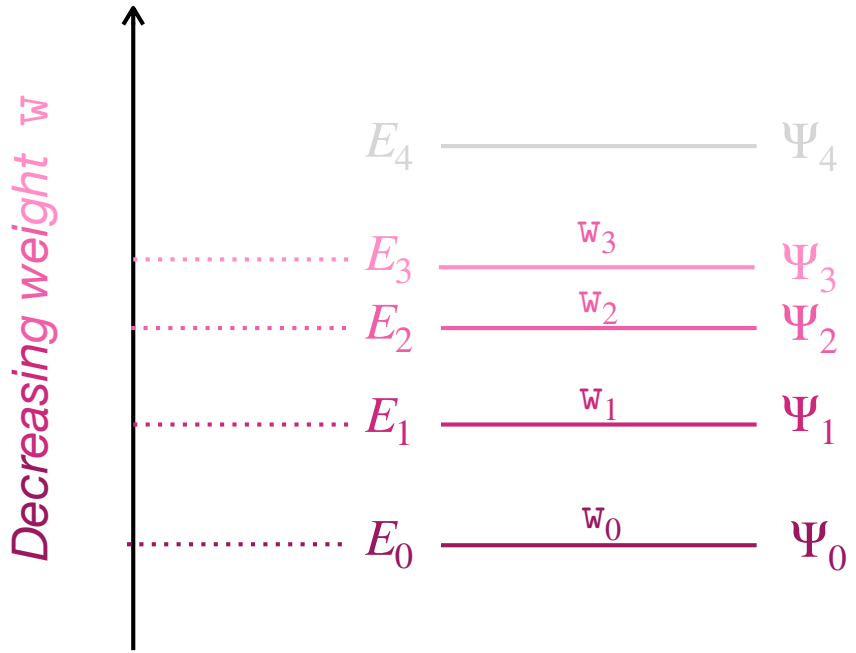
Theophilou-Gross-Oliveira-Kohn (TGOK) variational principle



$$w_0 \frac{\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle} + w_1 \frac{\langle \tilde{\Psi}_1 | \hat{H} | \tilde{\Psi}_1 \rangle}{\langle \tilde{\Psi}_1 | \tilde{\Psi}_1 \rangle} + \ldots + w_M \frac{\langle \tilde{\Psi}_M | \hat{H} | \tilde{\Psi}_M \rangle}{\langle \tilde{\Psi}_M | \tilde{\Psi}_M \rangle} \geq w_0 E_0 + w_1 E_1 + \ldots + w_M E_M$$

Orthogonal **trial** wave functions

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



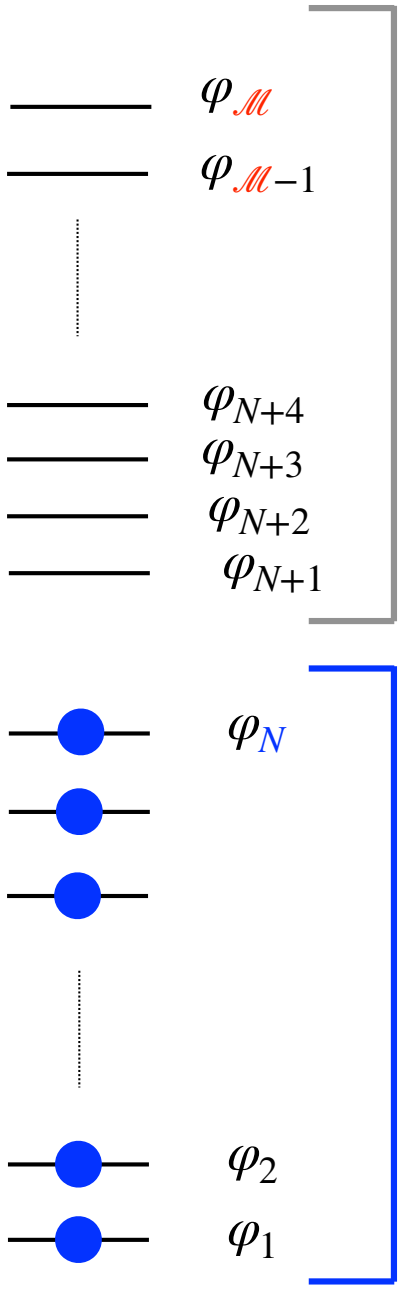
$$w_0 \frac{\langle \tilde{\Psi}_0 | \hat{H} | \tilde{\Psi}_0 \rangle}{\langle \tilde{\Psi}_0 | \tilde{\Psi}_0 \rangle} + w_1 \frac{\langle \tilde{\Psi}_1 | \hat{H} | \tilde{\Psi}_1 \rangle}{\langle \tilde{\Psi}_1 | \tilde{\Psi}_1 \rangle} + \ldots + w_M \frac{\langle \tilde{\Psi}_M | \hat{H} | \tilde{\Psi}_M \rangle}{\langle \tilde{\Psi}_M | \tilde{\Psi}_M \rangle} \geq w_0 E_0 + w_1 E_1 + \ldots + w_M E_M$$

Desired M lowest excited-state energies

Ground-state mean-field theory

(Hartree-Fock method)

From the one-electron to the many-electron problem



Virtual orbitals

$$|\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\mathrm{vac}\rangle \approx |\Psi_0\rangle$$

How do I find the occupied orbitals?

Hartree-Fock (mean-field) approximation

$$|\Psi_0\rangle \approx |\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\,\mathrm{vac}\rangle$$

Trial Slater determinant

$$E_0 \approx E_{\mathrm{HF}} = \min_{\Phi} \left\{ \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right\}$$

Total Hamiltonian in second quantisation

$$\hat{H} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \varphi_R \varphi_S \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Total Hamiltonian in second quantisation

$$\int d\mathbf{x}\, \varphi_P^*(\mathbf{x}) \left(-\frac{1}{2}\nabla_{\mathbf{r}}^2 + v_{\text{ne}}(\mathbf{r}) \right) \varphi_Q(\mathbf{x})$$

One-electron integrals

$$\hat{H} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \varphi_R \varphi_S \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Total Hamiltonian in second quantisation

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One-electron integrals

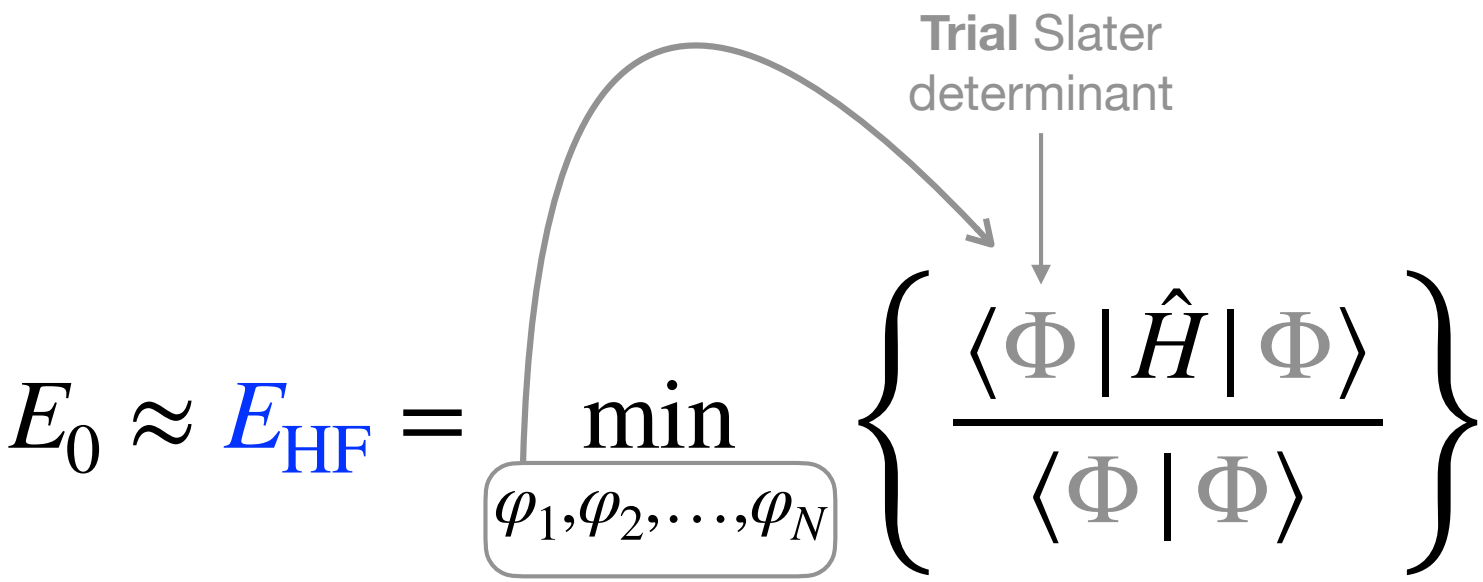
$$\hat{H} = \sum_{PQ} \langle \varphi_P | \hat{h} | \varphi_Q \rangle \hat{a}_P^\dagger \hat{a}_Q + \frac{1}{2} \sum_{PQRS} \langle \varphi_P \varphi_Q | \varphi_R \varphi_S \rangle \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_S \hat{a}_R$$

Two-electron integrals

$$\int d\mathbf{x}_1 \int d\mathbf{x}_2\, \varphi_P^*(\mathbf{x}_1) \varphi_Q^*(\mathbf{x}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_R(\mathbf{x}_1) \varphi_S(\mathbf{x}_2)$$

Hartree-Fock (mean-field) approximation

$$|\Psi_0\rangle \approx |\Phi_0\rangle \equiv \hat{a}_1^\dagger \hat{a}_2^\dagger \ldots \hat{a}_N^\dagger |\,\mathrm{vac}\rangle$$



$$E_0 \approx E_{\mathrm{HF}} = \min_{\varphi_1,\varphi_2,\ldots,\varphi_N} \left\{ \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right\}$$

$$=$$

$$\sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{i,j=1}^{N} \left(\langle ij | ij \rangle - \langle ij | ji \rangle \right)$$

$$h_{ij} = \int d\mathbf{x}\, \varphi_i^*(\mathbf{x}) \left(-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{ne}(\mathbf{r}) \right) \varphi_j(\mathbf{x})$$

One-electron integrals

$$E_0 \approx E_{\mathrm{HF}} = \min_{\varphi_1,\varphi_2,\ldots,\varphi_N} \left\{ \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right\}$$

$$\| $$

$$\sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{i,j=1}^{N} \left(\langle ij \,|\, ij \rangle - \langle ij \,|\, ji \rangle \right)$$

$$h_{ij} = \int d\mathbf{x}\, \varphi_i^*(\mathbf{x}) \left(-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{ne}(\mathbf{r}) \right) \varphi_j(\mathbf{x}) \longrightarrow \text{One-electron integrals}$$

$$\text{Two-electron integrals} \longleftarrow \langle ij \,|\, kl \rangle = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \, \frac{\varphi_i^*(\mathbf{x}_1) \varphi_j^*(\mathbf{x}_2) \varphi_k(\mathbf{x}_1) \varphi_l(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$E_0 \approx E_{\mathrm{HF}} = \min_{\varphi_1,\varphi_2,\ldots,\varphi_N} \left\{ \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \right\}$$

$$\Vert$$

$$\sum_{i=1}^{N} h_{ii} + \frac{1}{2} \sum_{i,j=1}^{N} \left(\langle ij \,|\, ij \rangle - \langle ij \,|\, ji \rangle \right)$$

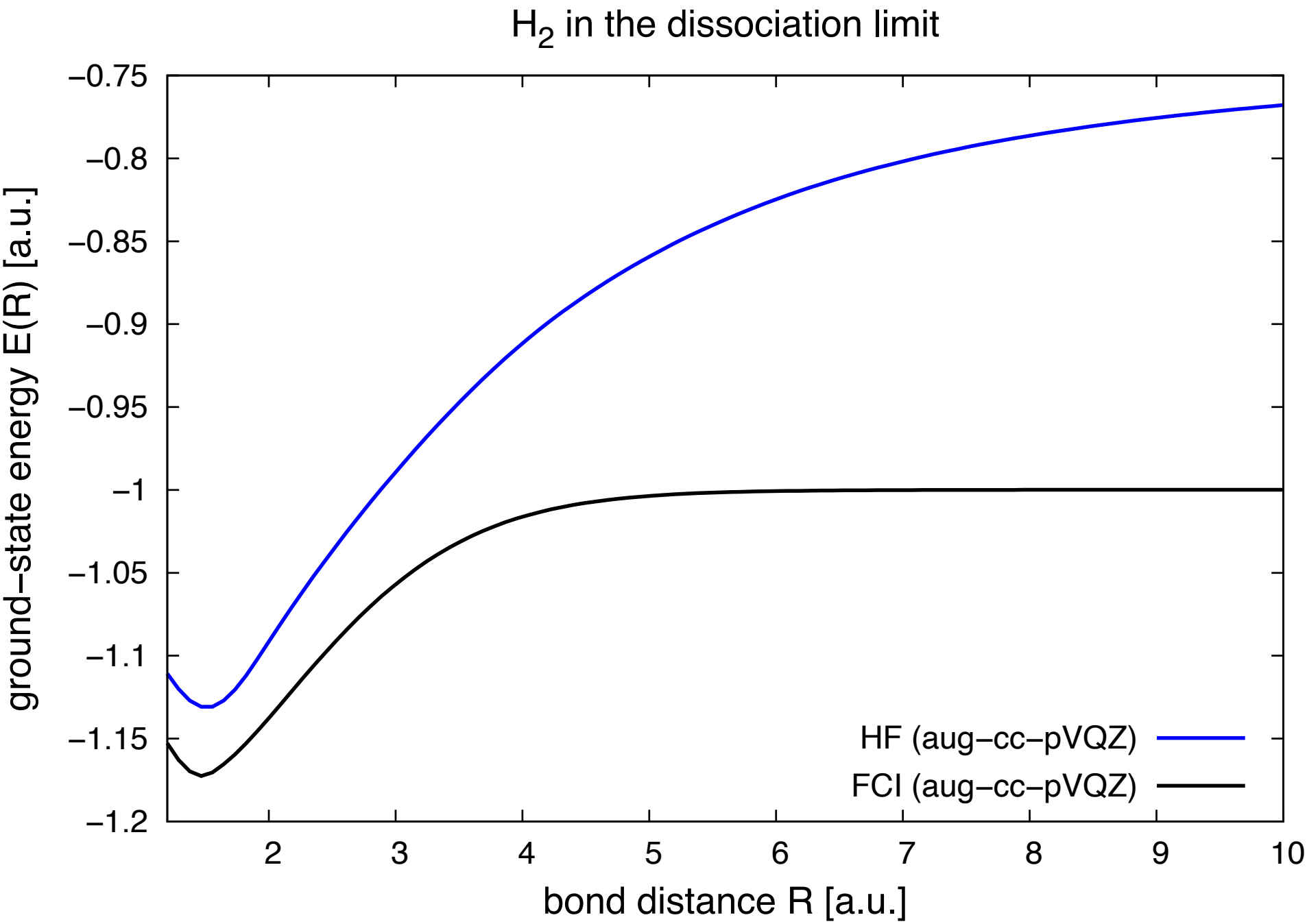
Coulomb (Hartree) energy

Exchange energy

$$h_{ij} = \int d\mathbf{x}\, \varphi_i^*(\mathbf{x}) \left(-\frac{\nabla_{\mathbf{r}}^2}{2} + v_{ne}(\mathbf{r}) \right) \varphi_j(\mathbf{x}) \longrightarrow \text{One-electron integrals}$$

$$\text{Two-electron integrals} \longleftarrow \langle ij \,|\, kl \rangle = \int d\mathbf{x}_1 \int d\mathbf{x}_2 \frac{\varphi_i^*(\mathbf{x}_1)\varphi_j^*(\mathbf{x}_2)\varphi_k(\mathbf{x}_1)\varphi_l(\mathbf{x}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

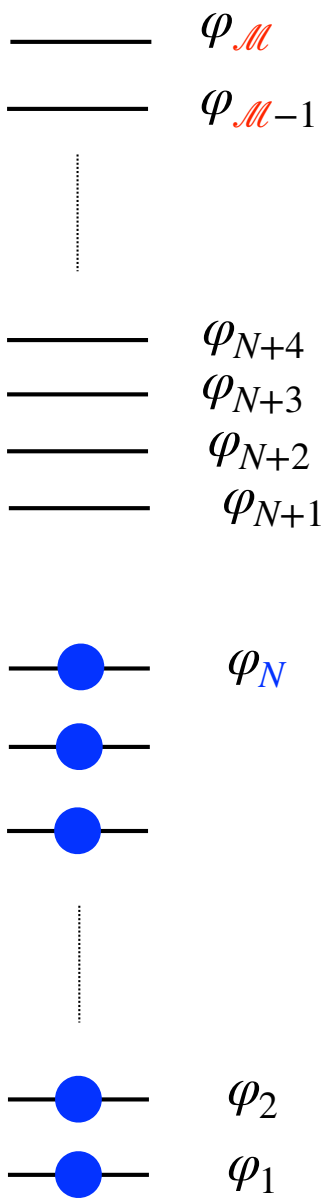
Hartree-Fock (mean-field) theory



Wavefunction theory

or how to describe electron correlation explicitly

Explicit description of electron correlation



Single, double, triple, quadruple, …, N-tuple excitations

Configuration Interaction (CI) method

Reference ground-state
HF determinant

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

Excitation operator

Configuration Interaction (CI) method

Reference ground-state
HF determinant

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

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

Configuration Interaction (CI) method

Reference ground-state
HF determinant

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

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

To-be-optimized CI coefficients

Configuration Interaction (CI) method

$$|\Psi_0\rangle \approx \hat{C}|\Phi_0\rangle = \boxed{\sum_{\xi} C_{\xi}|\det_{\xi}\rangle = |\Psi(\mathbf{C})\rangle}$$

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

To-be-optimized CI coefficients

Configuration Interaction (CI) method

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

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

Configuration Interaction (CI) method

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

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

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

Matrix diagonalization problem

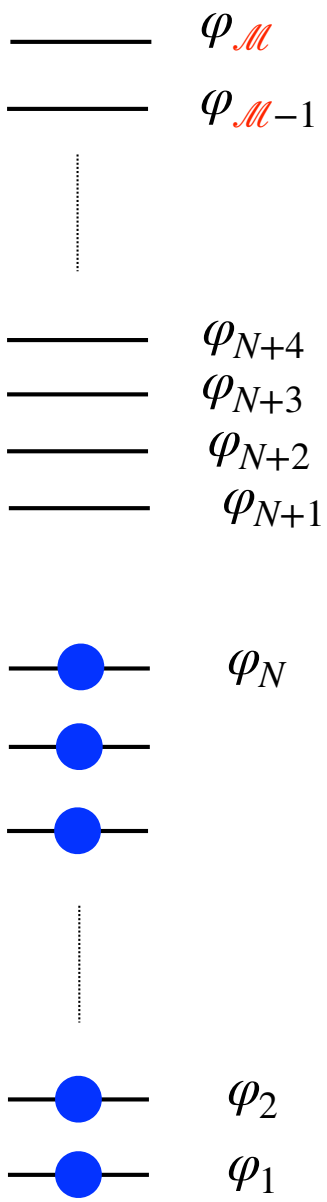
Configuration Interaction (CI) method

$$H_{\xi\xi'} = \langle \det_{\xi} | \hat{H} | \det_{\xi'} \rangle$$

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

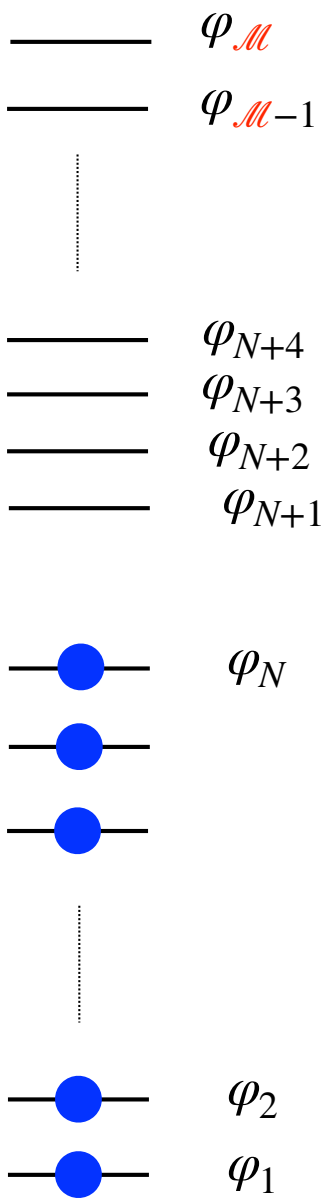
CI Hamiltonian matrix

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



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

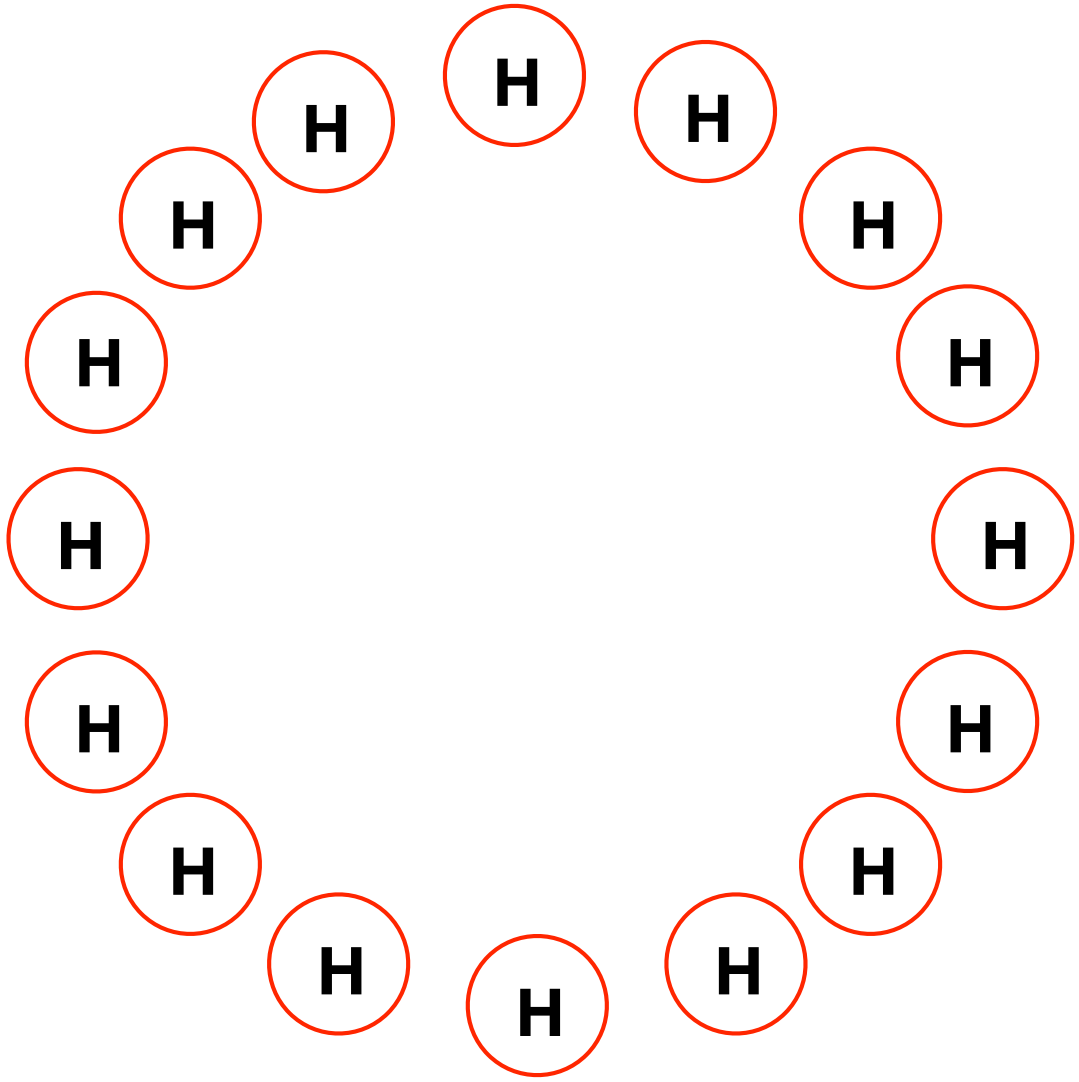
How many determinants in total?



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?

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

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

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

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?

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

A naive (important though) understanding of the "quantum advantage"

$$|\Psi_{\mathrm{FCI}}\rangle = \sum_{\xi} C_{\xi} |\det_{\xi}\rangle$$

- **Classical** encoding of all Slater determinants: $N_{\mathrm{det.}} \approx \dfrac{e^{2N \ln 2}}{\sqrt{\pi N}} \overset{N=50}{\approx} 10^{29}$

- The FCI wavefunction can in principle be encoded (in this example) with $\mathscr{M} = 2N$ **qubits**.

Exponential quantum advantage!

Coupled cluster theory:

A smarter encoding of electron correlation

Coupled Cluster (CC) theory

Reference ground-state
HF determinant

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

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

Excitation operator

Coupled Cluster (CC) theory

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

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

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

Coupled Cluster (CC) theory

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

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

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

CI

CC

Coupled Cluster (CC) theory

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

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

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

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

Find the CC amplitudes (i.e. $\hat{T}$) such that

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

Schrödinger equation for the CC wave function

Coupled Cluster (CC) theory

Not unitary!

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

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

Excitation operator

$$\hat{T}^\dagger \neq -\hat{T}$$

Unitary CC (uCC) theory

(standard in quantum algorithms for quantum chemistry)

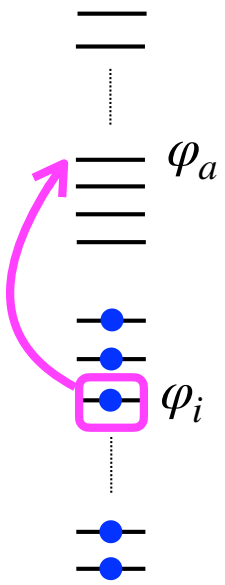
$$|\Psi_{\mathrm{CC}}(\mathbf{t})\rangle = e^{\hat{T}}|\Phi_0\rangle \quad \rightarrow \quad |\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle = e^{\hat{T}-\hat{T}^\dagger}|\Phi_0\rangle$$

Unitary CC (uCC) theory

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

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

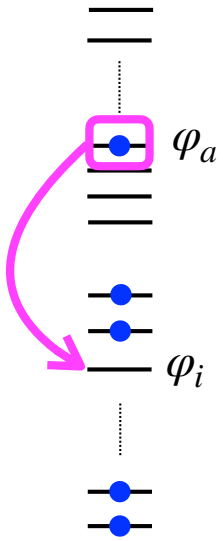
Excitation operator



Unitary CC (uCC) theory

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

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



De-excitation operator

*with the **same** CC amplitudes*

Unitary CC (uCC) theory

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

Unitary transformation

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

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

Unitary CC (uCC) theory

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

Unitary transformation

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

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

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Unitary CC (uCC) theory

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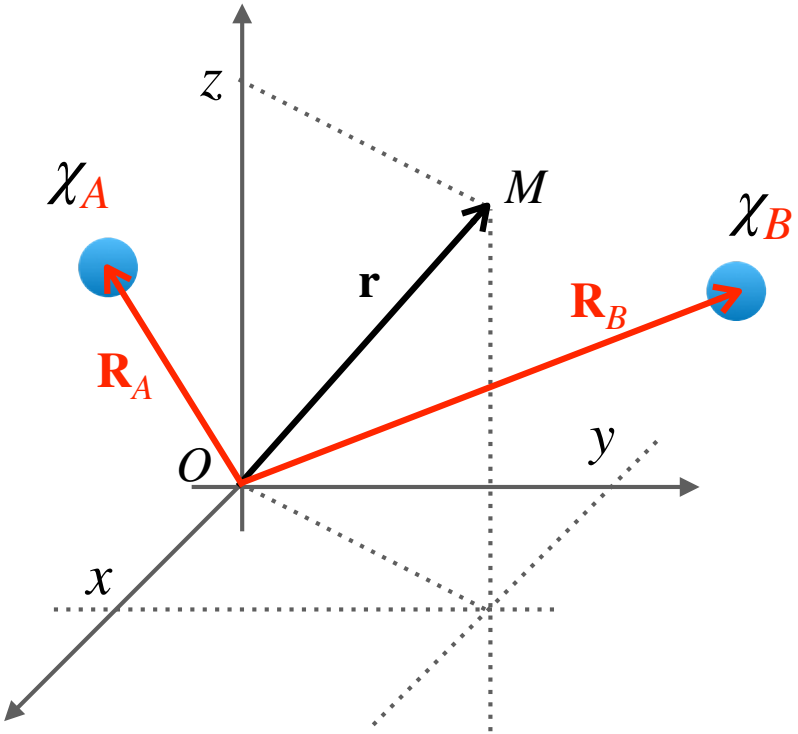
$$= \min_{\mathbf{t}} \left\{ \langle \Psi_{\mathrm{uCC}}(\mathbf{t})|\hat{H}|\Psi_{\mathrm{uCC}}(\mathbf{t})\rangle \right\}$$

Method of choice in **variational quantum eigensolvers** (VQE)!

Complements

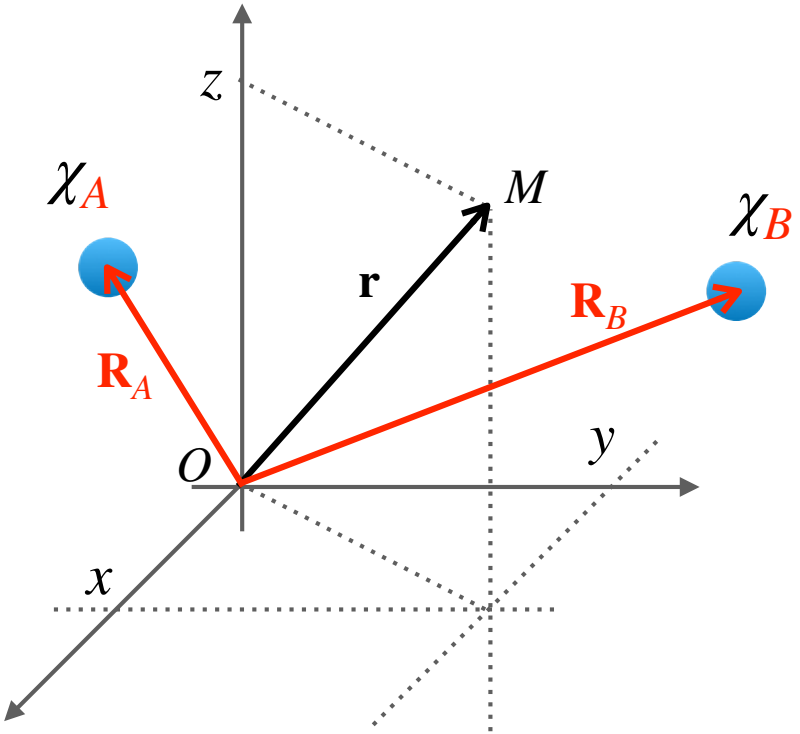
Molecular orbitals written as linear combinations of atomic orbitals



Atomic orbitals
(basis set)

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

Molecular orbitals written as linear combinations of atomic orbitals

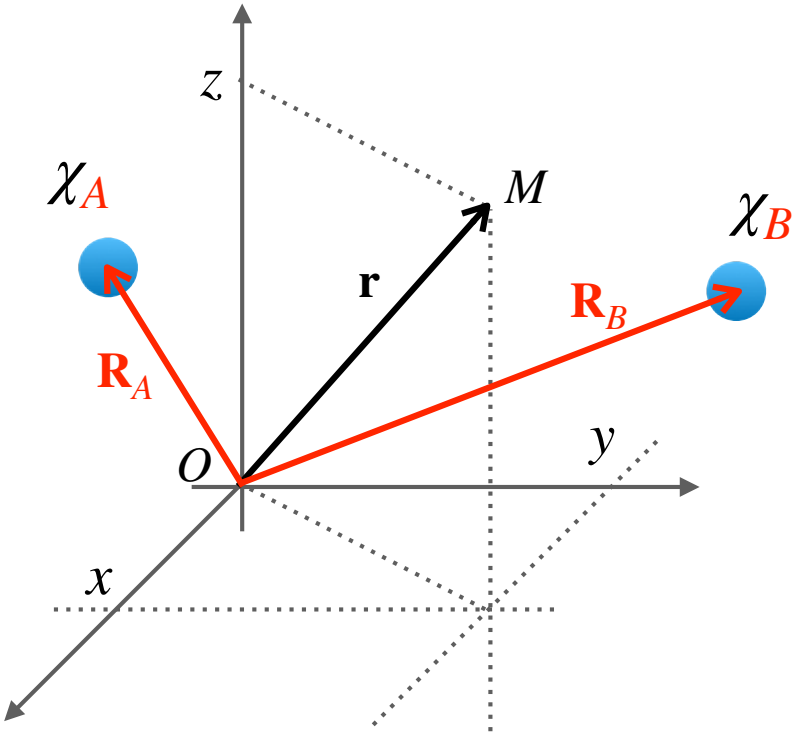


$$\varphi_p(\mathbf{r}) = C_{Ap}\,\chi_A(\mathbf{r}) + C_{Bp}\,\chi_B(\mathbf{r})$$

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

Atomic orbitals
(basis set)

Molecular orbitals written as linear combinations of atomic orbitals



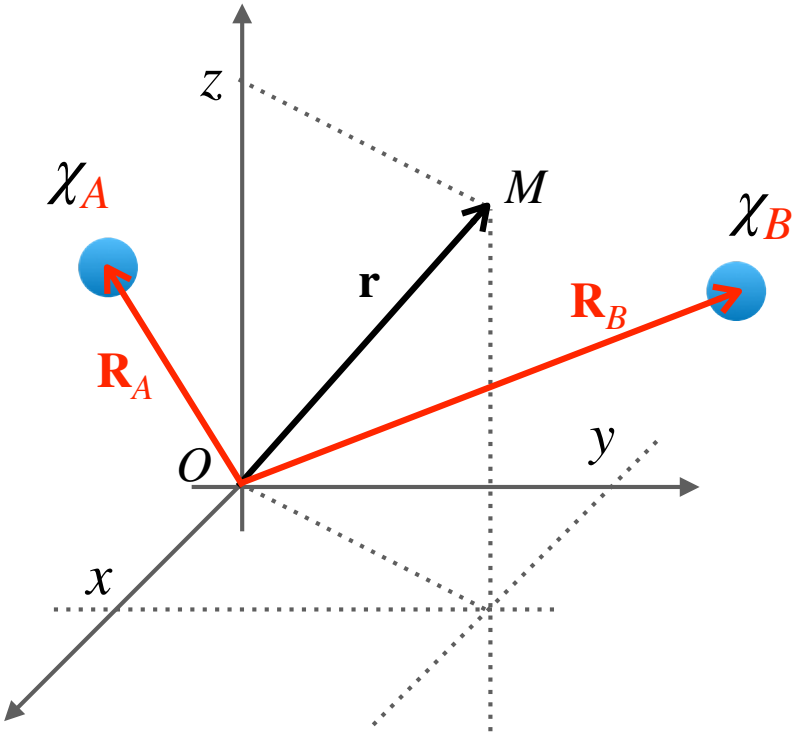
$$\varphi_p(\mathbf{r}) = C_{Ap}\,\chi_A(\mathbf{r}) + C_{Bp}\,\chi_B(\mathbf{r})$$

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

Optimized

molecular orbital coefficients

Molecular orbitals written as linear combinations of atomic orbitals



Size of the atomic orbital basis

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

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***

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

$e^{-\hat{T}}\times$

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

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

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

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

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

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

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***

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

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***

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

Effective N-electron Schrödinger equation

To-be-determined

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

Expansion ***stops exactly*** *at fourth order in* $\hat{T}$