SCF methods, basis sets, and integrals

Lecture I: Self-consistent field methods

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ESQC 2024, September 8 – 21, 2024

Preface

- Self-consistent field (SCF) or mean-field methods are widely used in physics to describe many-body problems.

- The idea is *not* to describe the interaction of one of the particles with all of the other particles individually and instantaneously, but rather only the interaction with the distribution of the particles.

- In the present course, we are concerned with the electrons in a molecule (not in the solid state), and the particles' distribution is the (total) molecular electron density $\rho(\mathbf{r})$.

- Since electrons possess spin, also the spin-density $\rho_s(\mathbf{r})$ may be relevant.

- The purpose of this course is to become familiar with the Hartree–Fock method using the LCAO expansion.

The molecular Hamiltonian

- Our aim is to solve the nonrelativistic time-independent Schrödinger equation of a molecular system (in S.I. units):

$$\hat{\tilde{H}}_{\mathrm{mol}}\tilde{\Psi}_k = \tilde{U}_k \tilde{\Psi}_k, \qquad k = 0, 1, 2, \dots$$

- In the absence of external (electric and magnetic) fields, the molecular Hamiltonian reads:

$$\hat{\tilde{H}}_{\mathrm{mol}} = \hat{\tilde{T}}_n + \hat{\tilde{T}}_e + \hat{\tilde{V}}_{nn} + \hat{\tilde{V}}_{ne} + \hat{\tilde{V}}_{ee}$$

- The kinetic energy operators are (in S.I. units):

$$\hat{\tilde{T}}_n = -\sum_{A=1}^{N} \frac{\hbar^2}{2\tilde{m}_A}\tilde{\Delta}_A, \qquad \hat{\tilde{T}}_e = -\sum_{\mu=1}^{n} \frac{\hbar^2}{2\tilde{m}_e}\tilde{\Delta}_\mu, \qquad \tilde{\Delta} = \left(\frac{\partial^2}{\partial \tilde{x}^2} + \frac{\partial^2}{\partial \tilde{y}^2} + \frac{\partial^2}{\partial \tilde{z}^2} \right)$$

The molecular Hamiltonian

- The Hamiltonian reads:

$$\hat{\tilde{H}}_{\text{mol}} = \hat{\tilde{T}}_n + \hat{\tilde{T}}_e + \hat{\tilde{V}}_{nn} + \hat{\tilde{V}}_{ne} + \hat{\tilde{V}}_{ee}$$

- The potential energy operators are (in S.I. units):

$$
\begin{aligned}
\hat{\tilde{V}}_{nn} &= \sum_{B=2}^{N}\sum_{A=1}^{B-1} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 |\tilde{\mathbf{r}}_A - \tilde{\mathbf{r}}_B|} = \sum_{B=2}^{N}\sum_{A=1}^{B-1} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0\, \tilde{r}_{AB}} \\
\hat{\tilde{V}}_{ne} &= -\sum_{A=1}^{N}\sum_{\nu=1}^{n} \frac{Z_A e^2}{4\pi\varepsilon_0 |\tilde{\mathbf{r}}_A - \tilde{\mathbf{r}}_\nu|} = -\sum_{A=1}^{N}\sum_{\nu=1}^{n} \frac{Z_A e^2}{4\pi\varepsilon_0\, \tilde{r}_{A\nu}} \\
\hat{\tilde{V}}_{ee} &= \sum_{\nu=2}^{n}\sum_{\mu=1}^{\nu-1} \frac{e^2}{4\pi\varepsilon_0 |\tilde{\mathbf{r}}_\mu - \tilde{\mathbf{r}}_\nu|} = \sum_{\nu=2}^{n}\sum_{\mu=1}^{\nu-1} \frac{e^2}{4\pi\varepsilon_0 \tilde{r}_{\mu\nu}}
\end{aligned}
$$

The molecular Hamiltonian: Simplifications

- We abbreviate summations as follows:

$$\sum_{\nu=2}^{n}\sum_{\mu=1}^{\nu-1} \to \sum_{\mu<\nu}, \qquad \sum_{A=1}^{N}\sum_{\nu=1}^{n} \to \sum_{A,\nu}$$

- We introduce atomic units, which simplify the equations drastically. Consider the dimensionless variable $r = \tilde{r}/a_0$, where a_0 is the Bohr radius, $a_0 = 52.917\,721\,0544(82)$ pm.

- The Coulomb repulsion between two electrons at a distance $\tilde{r}$ can then be written as:

$$\hat{\tilde{V}} = \frac{e^2}{4\pi\varepsilon_0\,\tilde{r}} = \frac{e^2}{4\pi\varepsilon_0\,r\,a_0}$$

- With $\hat{V} = \hat{\tilde{V}}/\left(e^2/4\pi\varepsilon_0\,a_0\right)$, we obtain: $\hat{V} = 1/r$.

Atomic units (a.u.)

- Also $\hat{V}$ is dimensionless!

- We abbreviate $e^2/4\pi\varepsilon_0\,a_0$ as E_{h}: Hartree, the unit of energy.
  $E_{\mathrm{h}} = 4.359\,744\,722\,2060(48) \times 10^{-18}$ J.

  Easy to remember: $\quad 0.04\,E_{\mathrm{h}} \cong 1\text{ eV} \cong 100\text{ kJ/mol} \cong 10{,}000\text{ cm}^{-1}$

- Hence, $\hat{V} = \hat{\tilde{V}}/E_{\mathrm{h}}$, or $\hat{\tilde{V}} = \hat{V} \times E_{\mathrm{h}}$.

- **What about kinetic energy?** The general kinetic energy operator is: $\hat{\tilde{T}} = -\hbar^2/(2\tilde{m})\tilde{\Delta}$.
  In terms of the dimensionless mass $m = \tilde{m}/m_e$ and dimensionless Laplacian
  $\Delta = a_0^2\tilde{\Delta}$, we obtain

  $$\hat{\tilde{T}} = -\frac{1}{2m}\left(\frac{\hbar^2}{m_e a_0^2}\right)\Delta$$

- Indeed, we find that $E_{\mathrm{h}} = \hbar^2/m_e a_0^2$ and hence, $\hat{T} = -\frac{1}{2m}\Delta$.

2022 CODATA recommended values (www.nist.gov)

Atomic unit	Symbol	Value		S.I. unit
of energy	E_h	4.359 744 722 2060(48)	$\times 10^{-18}$	J
of length	a_0	0.529 177 210 544(82)	$\times 10^{-10}$	m
of charge	e	1.602 176 634	$\times 10^{-19}$	C
of mass	m_e	9.109 383 7139(28)	$\times 10^{-31}$	kg
of action	$\hbar$	1.054 571 817 …	$\times 10^{-34}$	J s

... some derived atomic units:

Atomic unit	Symbol	Value	S.I. unit
of time	$\hbar/E_h$	$\approx 2.419 \times 10^{-17}$	s
of force	E_h/a_0	$\approx 8.239 \times 10^{-8}$	N
of current	$eE_h/\hbar$	$\approx 6.624 \times 10^{-3}$	A
of electric dipole moment	ea_0	$\approx 8.478 \times 10^{-30}$	C m
of magnetic dipole moment	$\hbar e/m_e$	$\approx 1.855 \times 10^{-23}$	J/T

Atomic units (a.u.)

- The dimensionless quantities without a tilde can be interpreted as quantities expressed in atomic units.

- From here on, we shall only work with these quantities!

- It's a good habit to report computational results with the proper symbols instead of "atomic units" or a.u.

- For example, it is better to report a computed first hyperpolarizability as "1.234 $e^3 a_0^3/E_{\mathrm{h}}^2$" than simply "1.234 a.u.".

The molecular Hamiltonian in atomic units

- Expectation values of the operator $\hat{S}^2$ are usually reported as plain numbers, for example, $\langle \hat{S}^2 \rangle = 0.75$. Should one add symbols? What is the value in S.I. units?

- An alternative way to introduce atomic units is to say that these are a system of units in which $\hbar = m_e = e = 4\pi\varepsilon_0 = 1$.

- In atomic units, the molecular Hamiltonian reads:

$$\hat{H}_{\text{mol}} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}, \quad \text{with}$$

$$\hat{T}_n = -\sum_A \frac{1}{2m_A} \Delta_A, \quad \hat{T}_e = -\sum_\mu \frac{1}{2} \Delta_\mu,$$

$$\hat{V}_{nn} = \sum_{A<B} \frac{Z_A Z_B}{r_{AB}}, \quad \hat{V}_{ne} = -\sum_{A,\nu} \frac{Z_A}{r_{A\nu}}, \quad \hat{V}_{ee} = \sum_{\mu<\nu} \frac{1}{r_{\mu\nu}}$$

The adiabatic approximation

- We are now ready to write Schrödinger's equation in atomic units,

$$\hat{H}_{\mathrm{mol}}\Psi_k = U_k\Psi_k, \qquad k = 0, 1, 2, \ldots$$

- The wavefunction Ψ_k depends on the positions of all particles and their spins,

$$\Psi_k \equiv \Psi_k(\mathbf{r}_A, \mathbf{r}_\mu, \text{nuclear spins}, \text{electron spins}), \quad \mathbf{r}_A \in \mathbb{R}^{3N}, \quad \mathbf{r}_\mu \in \mathbb{R}^{3n}$$

- In the adiabatic approximation, we write the total wavefunction as a product of a nuclear and an electronic wavefunction,

$$\Psi_k \approx \chi_K(\mathbf{r}_A, \text{nuclear spins}) \times \Phi_\kappa(\mathbf{r}_\mu, \text{electron spins}; \mathbf{r}_A)$$

For short,

$$\Psi_k = \chi_K \, \Phi_\kappa$$

Separation of centre-of-mass motion

- At this point, however, we realise that the function $\Psi_k = \chi_K \, \Phi_\kappa$ cannot be normalised since it contains the centre-of-mass (COM) motion, that is, the motion of the molecule as a whole.

- The COM coordinate is

$$\mathbf{R}_{\text{COM}} = \left\{ \sum_A m_A \mathbf{r}_A + \sum_\mu \mathbf{r}_\mu \right\} / M, \qquad M = n + \sum_A m_A$$

- The corresponding kinetic energy operator is:

$$\hat{T}_{\text{COM}} = -\frac{1}{2M} \Delta_{R_{\text{COM}}}, \qquad \hat{H}_{\text{relative}} = \hat{H} - \hat{T}_{\text{COM}}$$

- The wavefunction can be written as product of functions for relative and COM motion,

$$\Psi_{k,\text{total}} = \Psi_{k,\text{relative}} \, \xi_{\text{COM}}$$

The electronic Schrödinger equation

- We limit our attention to such $\hat{H}_{\text{relative}}$ that have bound-state solutions and we choose $\Psi_{k,\text{relative}}$ (normalised to unity) as a trial function to approximate a bound state of $\hat{H}_{\text{relative}}$.

- To proceed, we measure all of the coordinates relative to one of the nuclei, say $\mathbf{r}_X$,

$$\mathbf{q}_A = \mathbf{r}_A - \mathbf{r}_X \qquad \mathbf{q}_\mu = \mathbf{r}_\mu - \mathbf{r}_X$$

- We ignore spin for the moment and make the Born–Oppenheimer Ansatz

$$\Psi_{k,\text{relative}}(\mathbf{q}_A, \mathbf{q}_\mu) \approx \chi_K(\mathbf{q}_A) \times \Phi_\kappa(\mathbf{q}_\mu; \mathbf{q}_A), \;\; \mathbf{q}_A \in \mathbb{R}^{3(N-1)}, \;\; \mathbf{q}_\mu \in \mathbb{R}^{3n}$$

or, for short

$$\Psi_k = \chi_K \, \Phi_\kappa \qquad \text{same as before but with relative coordinates}$$

The electronic Schrödinger equation

- Using relative coordinates, we investigate the expectation value

$$E_{k,\text{relative}} = \langle \chi_K \, \Phi_\kappa | \hat{H}_{\text{relative}} | \chi_K \, \Phi_\kappa \rangle = \langle \chi_K \, \Phi_\kappa | \hat{H}_{\text{mol}} - \hat{T}_{\text{COM}} | \chi_K \, \Phi_\kappa \rangle$$

over the normalised wavefunction.

- Let us now assume that we have solved the electronic Schrödinger equation (SE) for clamped nuclei,

$$\left\{ \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} \right\} \Phi_\kappa(\mathbf{q}_\mu; \mathbf{q}_A) = E_\kappa \Phi_\kappa(\mathbf{q}_\mu; \mathbf{q}_A)$$

- We can then integrate over the electronic coordinates and obtain

$$E_{k,\text{relative}} \approx \langle \chi_K | \hat{T}_n + E_\kappa + \Delta E_\kappa | \chi_K \rangle$$

(This is the starting point for describing nuclear motion.)

The Born–Oppenheimer diagonal correction

- On the previous slide, we have encountered the Born–Oppenheimer diagonal correction (BODC)

$$\Delta E_\kappa = \langle \Phi_\kappa | \hat{T}_n | \Phi_\kappa \rangle$$

- This is the expectation value of the nuclear kinetic energy operator over the electronic wavefunction. In most of today's quantum-chemical calculations, the BODC is ignored (Born–Oppenheimer approximation). It's often a tiny correction.

- The electronic energy E_κ defines a potential-energy (hyper)surface (PES). It is independent of the nuclear masses and hence equal for all isotopic species.

- ΔE_κ, however, does depend on the nuclear masses and thus, the sum $E_\kappa + \Delta E_\kappa$ defines an isotope-dependent PES.

The hydrogen atom

- The H atom has only one nucleus with coordinate $\mathbf{r}_P$. Solving the ground-state ($\kappa = 0$) electronic SE yields:

$$\Phi_0(\mathbf{r}) = \frac{1}{\sqrt{\pi}} \exp(-|\mathbf{r} - \mathbf{r}_P|), \quad E_0 = -0.500\,000\,0\ E_{\mathrm{h}}$$

- The BODC to the ground-state energy is:

$$\Delta E_0 = \langle \Phi_0 | \hat{T}_n | \Phi_0 \rangle = \frac{1}{2m_P} = 0.000\,272\,3\ E_{\mathrm{h}}$$

- We thus find $E_0 + \Delta E_0 = -0.499\,727\,7\ E_{\mathrm{h}}$, which is in almost full agreement with the exact energy $E_{0,\mathrm{exact}} = -0.499\,727\,8\ E_{\mathrm{h}}$.

- Note that, in terms of the reduced mass $m_{\mathrm{red}} = m_P/(1 + m_P)$,

$$E_{0,\mathrm{exact}} = -\frac{1}{2} m_{\mathrm{red}} = -\frac{1}{2}\left(1 - \frac{1}{m_P} + \frac{1}{m_P^2} - \cdots\right)$$

The potential energy (hyper)surface (PES)

- The BO approximation is an excellent approximation.

- It defines a mass-independent E_κ and a small mass-dependent correction ΔE_κ (usually ignored).

- The BO approximation defines the potential (hyper)surface and justifies ("explains") the separation of UV/Vis, IR, and microwave spectra.

- Treatment of $\hat{H}\Phi_\kappa = E_\kappa \Phi_\kappa$ is central to quantum chemistry
  — it's a formidable problem.
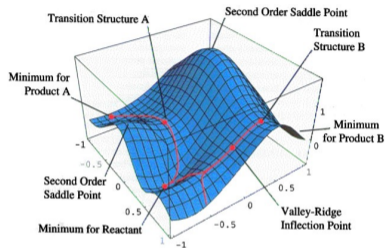
- Methods are available to locate stationary points (minima, saddle points) on the PES.

The electronic Schrödinger equation

- The electronic SE reads:

$$\hat{H}\Phi_\kappa = E_\kappa \Phi_\kappa, \qquad \text{with } \hat{H} = T_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee}$$

- In the following, we are only concerned with the electronic Hamiltonian $\hat{H}$.

- However, the exact solution of the electronic SE is hopeless.

- Therefore, we shall apply the variation method,

$$E[\Phi] = \langle\Phi|\hat{H}|\Phi\rangle/\langle\Phi|\Phi\rangle \geq E_0, \qquad \delta_\Phi E[\Phi] = 0 \leftrightarrow \Phi = \text{exact}$$

- If the energy functional (*i.e.*, the expectation value) is stationary with respect to all possible variations δ_Φ in the function Φ, then Φ is the exact solution.

Approximate solutions

- Concerning the variation method,

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle / \langle \Phi | \Phi \rangle \geq E_0, \qquad \delta_\Phi E[\Phi] = 0 \leftrightarrow \Phi = \text{exact}$$

we guess an Ansatz Φ and do a limited variation.

- Main problem: $E[\Phi]$ requires $3n$-dimensional integration since Φ is a function of the $3n$ electronic coordinates.

- For example, if the wavefunction is expanded using exponentially correlated Gaussians (ECG), then $3n$-dimensional integrals must be evaluated,

$$\chi_{\text{ECG}} = \exp\left(-\sum_\mu a_\mu |\mathbf{r}_\mu - \mathbf{C}_\mu|^2 - \sum_{\mu < \nu} b_{\mu\nu} |\mathbf{r}_\mu - \mathbf{r}_\nu|^2\right)$$

- Today, the ECG approach is limited to molecules with at most six electrons.

The Hartree product Θ for two electrons

- We consider the function $\Theta(1,2) = \varphi_1(1)\varphi_2(2)$. This is the Hartree product. Electron 1 is in orbital 1, electron 2 is in (another) orbital 2. The orbitals are normalised to unity.

- This Hartree product contradicts the indistinguishability of electrons and is hence not acceptable as a wavefunction.

- Furthermore, we ignore electron spin.

- Nevertheless, it is worth computing the expectation value of the Hartree product and to apply the variation method,

$$\langle\Theta|\hat{H}|\Theta\rangle = h_{11} + h_{22} + \langle 12|12\rangle + V_{nn}$$

$$h_{ii} = \langle\varphi_i|\hat{h}|\varphi_i\rangle = \int \varphi_i^*(\mathbf{r})\left(-\tfrac{1}{2}\Delta - \sum_A \frac{Z_A}{|\mathbf{r}-\mathbf{r}_A|}\right)\varphi_i(\mathbf{r})d\mathbf{r}$$

The Hartree product Θ for two electrons

- For a two-electron system, the expectation value of the Hartree product is

$$\langle\Theta|\hat{H}|\Theta\rangle = h_{11} + h_{22} + \langle 12|12\rangle + V_{nn}$$

$$\langle 12|12\rangle = \int\int \varphi_1^*(\mathbf{r})\varphi_2^*(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\varphi_1(\mathbf{r})\varphi_2(\mathbf{r}')d\mathbf{r}d\mathbf{r}'$$

- How is the above expression derived?

- First, we note that

$$\hat{H} = \hat{T}_e + \hat{V}_{nn} + \hat{V}_{ne} + \hat{V}_{ee} = \hat{h}_1 + \hat{h}_2 + \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} + \hat{V}_{nn}$$

$$\hat{h}_\mu = -\tfrac{1}{2}\Delta_\mu - \sum_A \frac{Z_A}{|\mathbf{r}_\mu - \mathbf{r}_A|}, \qquad \hat{H} = \hat{V}_{nn} + \sum_\mu \hat{h}_\mu + \sum_{\mu<\nu} r_{\mu\nu}^{-1}$$

The Hartree product Θ for two electrons

- We thus have evaluated the following integrals:

$$
\begin{aligned}
\langle\Theta|\hat{h}_1|\Theta\rangle &= \langle\varphi_1|\hat{h}_1|\varphi_1\rangle_1 \times \langle\varphi_2|\varphi_2\rangle_2 = \langle\varphi_1|\hat{h}|\varphi_1\rangle = h_{11} \\
\langle\Theta|\hat{h}_2|\Theta\rangle &= \langle\varphi_1|\varphi_1\rangle_1 \times \langle\varphi_2|\hat{h}_2|\varphi_2\rangle_2 = \langle\varphi_2|\hat{h}|\varphi_2\rangle = h_{22} \\
\langle\Theta|r_{12}^{-1}|\Theta\rangle &= \langle 12|12\rangle \\
\langle\Theta|\hat{V}_{nn}|\Theta\rangle &= V_{nn}
\end{aligned}
$$

- Next, we change φ_1 into $\varphi_1 + \delta$ (with $\langle\varphi_1|\delta\rangle = 0$) and require that the terms linear in δ vanish (variation method),

$$
\langle(\varphi_1 + \delta)\varphi_2|\hat{H}|(\varphi_1 + \delta)\varphi_2\rangle = \langle\Theta|\hat{H}|\Theta\rangle + \langle\delta\varphi_2|\hat{H}|\Theta\rangle + \langle\Theta|\hat{H}|\delta\varphi_2\rangle + \mathcal{O}(\delta^2)
$$

- This yields

$$
\langle\delta\varphi_2|\hat{H}|\Theta\rangle = 0 \quad \text{and} \quad \langle\Theta|\hat{H}|\delta\varphi_2\rangle = 0
$$

The Hartree product Θ for two electrons

- We evaluate $\langle \delta\varphi_2 | \hat{H} | \Theta \rangle$ and its complex conjugate (c.c.),

$$
\begin{aligned}
\langle \delta\varphi_2 | \hat{H} | \varphi_1\varphi_2 \rangle &= \langle \delta | \hat{h} | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle + \langle \delta | \varphi_1 \rangle \langle \varphi_2 | \hat{h} | \varphi_2 \rangle + \langle \delta\varphi_2 | \varphi_1\varphi_2 \rangle \\
&= \langle \delta | \hat{h} | \varphi_1 \rangle + \langle \delta\varphi_2 | \varphi_1\varphi_2 \rangle = \langle \delta | \hat{h} + \hat{J}_2 | \varphi_1 \rangle
\end{aligned}
$$

  with

$$
\hat{J}_2(\mathbf{r}) = \int \frac{\varphi_2^*(\mathbf{r}')\varphi_2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
$$

- Analogously,

$$
\langle \varphi_1\varphi_2 | \hat{H} | \delta\varphi_2 \rangle = \langle \varphi_1 | \hat{h} + \hat{J}_2 | \delta \rangle
$$

- Thus, we find that the "best orbital φ_1" in the sense of the variation principle is the orbital that satisfies

$$
\langle \delta | \hat{h} + \hat{J}_2 | \varphi_1 \rangle = 0 \quad \text{and} \quad \langle \varphi_1 | \hat{h} + \hat{J}_2 | \delta \rangle = 0
$$

The Coulomb operator

- We have encountered the operator

$$\hat{J}_2(\mathbf{r}) = \int \frac{\varphi_2^*(\mathbf{r}')\varphi_2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- $\hat{J}_2$ is the Coulomb operator. It is the potential generated by the charge distribution $\varphi_2^*(\mathbf{r}')\varphi_2(\mathbf{r}')$. Note that the "2" on $\hat{J}_2$ refers to the "*orbital 2*", not to the "*electron 2*".

- In general, we may write

$$\hat{J}_k(\mathbf{r}) = \int \frac{\varphi_k^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- Furthermore, if we change φ_2 into $\varphi_2 + \delta$, we obtain

$$\langle\delta|\hat{h} + \hat{J}_1|\varphi_2\rangle = 0 \quad \text{and} \quad \langle\varphi_2|\hat{h} + \hat{J}_1|\delta\rangle = 0$$

The Hartree equations for two electrons

- We find that the two orbitals φ_1 and φ_2 must be eigenfunctions to the operators $\hat{h} + \hat{J}_2$ and $\hat{h} + \hat{J}_1$, respectively:

$$\left(\hat{h} + \hat{J}_2\right)|\varphi_1\rangle = \hat{F}_1|\varphi_1\rangle = \varepsilon_1|\varphi_1\rangle$$

$$\left(\hat{h} + \hat{J}_1\right)|\varphi_2\rangle = \hat{F}_2|\varphi_2\rangle = \varepsilon_2|\varphi_2\rangle$$

- The two orbitals are eigenfunctions to *different operators*. The Coulomb potential is only due to the *other orbital*. This is *not so* in the Hartree–Fock method, as we shall see later.

- The operators $\hat{F}_k$ $(k = 1, 2)$ depend on the orbitals, and thus, the equations must be solved in an iterative manner.

- The two-electron Hartree method can easily be generalised to any number of (distinguishable and spin-free) particles.

The Hartree equations for many electrons

- For three electrons, we find

$$\langle \varphi_1 \varphi_2 \varphi_3 | \hat{H} | \varphi_1 \varphi_2 \varphi_3 \rangle = V_{nn} + h_{11} + h_{22} + h_{33} + \langle 12|12 \rangle + \langle 13|13 \rangle + \langle 23|23 \rangle$$

- In general, we find

$$\langle \Theta | \hat{H} | \Theta \rangle = V_{nn} + \sum_i h_{ii} + \sum_{i<j} \langle ij|ij \rangle$$

- It follows from the variation $\varphi_m \to \varphi_m + \delta$ that

$$\hat{F}_m | \varphi_m \rangle = \varepsilon_m | \varphi_m \rangle, \quad \text{with} \quad \hat{F}_m = \hat{h} + \sum_{k \neq m} \int \frac{\varphi_k^*(\mathbf{r}')\varphi_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- Note that the orbital m is excluded from the above sum.

KIT

Pauli exclusion principle

- The Hartree product is inacceptable as electronic wavefunction.

- Electrons are identical particles and there should be no detectable change in any of the observable properties of the molecule if the identical particles were to be interchanged.

- For a system of identical particles, the wavefunction must obey

$$\hat{P}_{\mu\nu}\Phi(1\ldots\mu\ldots\nu\ldots n) = \pm\Phi(1\ldots\nu\ldots\mu\ldots n)$$

- For fermionic systems, we accept as a postulate that

$$\hat{P}_{\mu\nu}\Phi(1\ldots\mu\ldots\nu\ldots n) = -\Phi(1\ldots\nu\ldots\mu\ldots n)$$

- Pauli exclusion principle: "A many-electron wavefunction must be antisymmetric with respect to interchange of the coordinates of any two electrons."

Permutations

- The permutations $P : (12 \ldots n) \Rightarrow (ij \ldots k)$ form the symmetric group of order $n!$

- The transposition P_{ij} interchanges the integers i and j.

- Every P can be represented as a product of p transpositions (in different ways).

- The parity δP of the permutation P is defined as $\delta P = (-1)^p$.

- It is easily verified that

$$\delta(P^{-1}) = \delta P, \qquad \delta(PQ) = \delta P \delta Q$$

- A permutation P describes a mapping of n-electron coordinate space, $x = (1 \ldots n)$, onto itself

$$Px = P(1 \ldots n) = y$$

Permutation operators

- The permutation P that describes a mapping of n-electron coordinate space onto itself, $Px = y$, induces an operator $\hat{P}$ in function space as follows:

$$\hat{P}\phi(x) = \phi(P^{-1}x) = \psi(x)$$

- The operators $\hat{P}$ are unitary operators, $\hat{P}^\dagger = \hat{P}^{-1}$ and have the same algebra as the permutations,

$$PQ = R \Rightarrow \hat{P}\hat{Q} = \hat{R}$$

- The crucial operator for many-electron systems is the antisymmetriser $\hat{\mathcal{A}}$,

$$\hat{\mathcal{A}} = \sum_P \delta P \, \hat{P} = \sum_P (-1)^p \hat{P} = \sum_P (-1)^p \hat{P}^{-1}$$

- $\hat{\mathcal{A}}$ is hermitean ($\hat{\mathcal{A}}^\dagger = \hat{\mathcal{A}}$).

The antisymmetriser $\hat{\mathcal{A}}$

- Applied to an arbitrary function Θ, we obtain

$$\hat{P}_{\mu\nu}(\hat{\mathcal{A}}\Theta) = -(\hat{\mathcal{A}}\Theta)$$

  Thus, $(\hat{\mathcal{A}}\Theta)$ always obeys the Pauli exclusion principle.

- Let $\hat{O}$ be a totally symmetric n-electron operator such as the electronic Hamiltonian $\hat{H}$. Then,

$$[\hat{\mathcal{A}}, \hat{O}] = 0$$

- Using the antisymmetriser, we can obtain an acceptable electronic wavefunction from the Hartree product as follows:

$$\Phi = C\hat{\mathcal{A}}\Theta, \quad \text{where } C \text{ is a normalisation constant}$$

- Φ is usually referred to as Slater determinant.

The Slater determinant (SD)

- We define, for given orbitals φ_i and coordinates $\mathbf{r}_\mu$, the matrix

$$\boldsymbol{\varphi} : \varphi_{i\mu} = \varphi_i(\mu) = \varphi_i(\mathbf{r}_\mu)$$

Then, Φ can be written as

$$\Phi = C\hat{A}\Theta = C \det(\boldsymbol{\varphi})$$

- Usually, we abbreviate the SD in the following manner:

$$\Phi = C \det(\boldsymbol{\varphi}) = C \begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(n) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(n) \\ \vdots & & & \vdots \\ \varphi_n(1) & \varphi_n(2) & \dots & \varphi_n(n) \end{vmatrix} = |\varphi_1\varphi_2\varphi_3\dots\varphi_n\rangle$$

Note that the notation $|\varphi_1\varphi_2\varphi_3\dots\varphi_n\rangle$ includes the normalisation constant (and so does Φ).

Properties of determinant wavefunctions

- SD's are, up to a constant, invariant under linear transformations of the MOs,

$$\tilde{\boldsymbol{\varphi}} : \tilde{\varphi}_i(\mathbf{r}_\mu) = \sum_{j=1}^{n} \varphi_j(\mathbf{r}_\mu) V_{ji} \;\Rightarrow\; \det(\tilde{\boldsymbol{\varphi}}) = \det(\boldsymbol{\varphi}) \det(\mathbf{V})$$

  Hence, we shall assume in the following that the MOs are orthonormal (in contrast with valence-bond theory, VB).

- Then, the normalisation constant is $C = (n!)^{-\frac{1}{2}}$, which follows from requiring that

$$\langle \Phi | \Phi \rangle = C^2 \langle \hat{\mathcal{A}}\Theta | \hat{\mathcal{A}}\Theta \rangle = n! C^2 \langle \Theta | \hat{\mathcal{A}}\Theta \rangle = n! C^2 = 1$$

  where we have used $\hat{\mathcal{A}}^2 = n! \hat{\mathcal{A}}$.

- Although the SD consists of $n!$ terms, the $3n$-dimensional integration is not difficult. We shall use orthonormal MOs and the property $\hat{\mathcal{A}}^2 = n! \hat{\mathcal{A}}$.

Expectation values over a SD

- The expectation value over the nuclear repulsion operator is a trivial zero-electron term,

$$\langle\Phi|\hat{V}_{nn}|\Phi\rangle = V_{nn} = \sum_{A<B} \frac{Z_A Z_B}{r_{AB}}$$

- The expectation value of the one-electron part of the Hamiltonian is also easy to compute (note that $\Phi = C\hat{A}\Theta$),

$$\langle\Phi|\sum_\mu \hat{h}_\mu|\Phi\rangle = C^2\langle\hat{A}\Theta|\sum_\mu \hat{h}_\mu|\hat{A}\Theta\rangle = C^2\langle\hat{A}^2\Theta|\sum_\mu \hat{h}_\mu|\Theta\rangle$$

$$= C^2\, n!\,\langle\hat{A}\Theta|\sum_\mu \hat{h}_\mu|\Theta\rangle = \langle\hat{A}\Theta|\sum_\mu \hat{h}_\mu|\Theta\rangle = \langle\Theta|\sum_\mu \hat{h}_\mu|\Theta\rangle$$

Note that $\hat{A}$ commutes with the Hamiltionian and that the turn-over rule can be applied. Furthermore, only the identity permutation survives.

Expectation values over a SD

- The expectation value of the two-electron part of the Hamiltonian is not more difficult to compute than the one-electron part,

$$\langle\Phi|\sum_{\mu<\nu} r_{\mu\nu}^{-1}|\Phi\rangle = \langle\Theta|\sum_{\mu<\nu} r_{\mu\nu}^{-1}|\hat{\mathcal{A}}\Theta\rangle = \sum_{\mu<\nu}\langle\Theta|r_{\mu\nu}^{-1}|\hat{\mathcal{A}}\Theta\rangle$$

- Only the identity permutation and the transposition $\hat{P}_{\mu\nu}$ survive,

$$\langle\Phi|\sum_{\mu<\nu} r_{\mu\nu}^{-1}|\Phi\rangle = \sum_{\mu<\nu}\langle\Theta|r_{\mu\nu}^{-1}|(1-\hat{P}_{\mu\nu})\Theta\rangle$$

- The final result is

$$\langle\Phi|\hat{H}|\Phi\rangle = V_{nn} + \sum_i h_{ii} + \sum_{i<j}\langle ij||ij\rangle$$

with $\langle ij||ij\rangle = \langle ij|ij\rangle - \langle ij|ji\rangle$.

Hartree *versus* Hartree–Fock

- The expectation value of the Hartree product Θ was:

$$\langle\Theta|\hat{H}|\Theta\rangle = V_{nn} + \sum_i h_{ii} + \sum_{i<j} \langle ij|ij\rangle$$

- The Hartree–Fock expectation value of the SD is:

$$\langle\Phi|\hat{H}|\Phi\rangle = V_{nn} + \sum_i h_{ii} + \sum_{i<j} \langle ij||ij\rangle$$

- The expectation values look very similar, but note that:

  1. The Hartree product is inacceptable for electrons.
  2. The Hartree–Fock orbitals must be chosen orthogonal to give a simple result.
  3. $\hat{H}$ is the exact nonrelativistic, clamped-nuclei Hamiltonian. The only approximation that we have invoked so far has been the wavefunction being a single determinant.

The Hartree–Fock equations

- A SD seems a reasonable approximation for the many-electron wavefunction, but we still have to determine the orbitals (MOs).

- As before for the Hartree method, we change φ_k into $\varphi_k + \delta$ (with $\langle \varphi_m | \delta \rangle = 0 \ \forall \ m$) and require that the terms linear in δ vanish (variation method). We do so for all k.

- Before we do so, we write the Hartree–Fock expectation value $E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle$ as

$$E[\Phi] = V_{nn} + \sum_i h_{ii} + \sum_{i<j} \langle ij || ij \rangle = V_{nn} + \sum_i h_{ii} + \tfrac{1}{2} \sum_{i,j} \langle ij || ij \rangle$$

- The first-order variation $\delta_k^{(1)} E[\Phi]$ becomes

$$\delta_k^{(1)} E[\Phi] = h_{\delta k} + \tfrac{1}{2} \sum_j \langle \delta j || kj \rangle + \tfrac{1}{2} \sum_i \langle i\delta || ik \rangle + \text{c.c.}$$

The Hartree–Fock equations

- Of course, we can add the last two sums and obtain

$$\delta_k^{(1)} E[\Phi] = h_{\delta k} + \sum_m \langle m\delta || mk \rangle + \text{c.c.} = F_{\delta k} + \text{c.c.} = 0$$

- Here, we have defined the Fock operator (p, q arbitrary),

$$F_{pq} = \langle \varphi_p | \hat{F} | \varphi_q \rangle = \langle \varphi_p | \hat{h} + \hat{J} - \hat{K} | \varphi_q \rangle = h_{pq} + \sum_m \langle mp | mq \rangle - \sum_m \langle mp | qm \rangle$$

- This equation in turn defines the Coulomb operator $\hat{J}$ and the exchange operator $\hat{K}$ via their matrix elements,
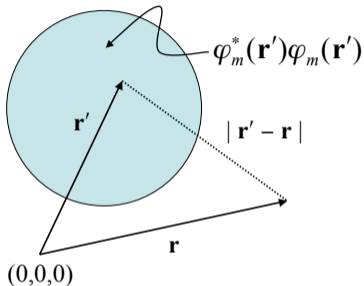
$$J_{pq} = \langle \varphi_p | \hat{J} | \varphi_q \rangle = \sum_m \langle mp | mq \rangle, \qquad K_{pq} = \langle \varphi_p | \hat{K} | \varphi_q \rangle = \sum_m \langle mp | qm \rangle$$

The Coulomb operator

- We can write the Coulomb operator as

$$\hat{J} = \sum_m \hat{J}_m = \sum_m \int \frac{\varphi_m^*(\mathbf{r}')\varphi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'$$

- The Coulomb operator is a multiplicative local operator. $\hat{J}_m$ is the electrostatic potential from the charge distribution $\varphi_m^*\varphi_m$.

- The total Coulomb operator $\hat{J}$ is the electrostatic potential from the total electron distribution in the molecule. Thus, an electron that "feels" this potential interacts with itself (*self-interaction*).

The exchange operator

- The exchange operator is much more difficult to interpret than the Coulomb operator. It does not occur in the Hartree method.

- It has its pure quantum mechanical origin in the need for an antisymmetric wavefunction for non-distinguishable fermions.

- It is a non-local, integral operator, defined by its action on an arbitrary function $f(\mathbf{r})$,

$$\hat{K} f(\mathbf{r}) = \sum_m \hat{K}_m f(\mathbf{r}) = \sum_m \left[\int \frac{\varphi_m^*(\mathbf{r}') f(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] \varphi_m(\mathbf{r}) = g(\mathbf{r})$$

- The (local) Coulomb operator can be defined analogously,

$$\hat{J} f(\mathbf{r}) = \sum_m \hat{J}_m f(\mathbf{r}) = \sum_m \left[\int \frac{\varphi_m^*(\mathbf{r}') \varphi_m(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \right] f(\mathbf{r}) = J(\mathbf{r}) f(\mathbf{r})$$

The Coulomb and exchange operators

- For any point $\mathbf{r}$ in space, we can ask for the value of the Coulomb potential $J(\mathbf{r})$. We can give this value in atomic units in E_h/e or in S.I. units in J/C (joules per coulomb).

- An important action of the exchange operator in Hartree–Fock theory is that it cancels the (unphysical) self-interaction $\langle kk|kk \rangle$ that occurs in the Coulomb operator,

$$
\begin{aligned}
\langle \varphi_k | \hat{J} - \hat{K} | \varphi_k \rangle &= \sum_m \left(\langle mk|mk \rangle - \langle mk|km \rangle \right) \\
&= \sum_{m \neq k} \left(\langle mk|mk \rangle - \langle mk|km \rangle \right)
\end{aligned}
$$

- In density-functional theory (DFT), the self-interaction causes big problems.

The Hartree–Fock equations

- We had derived before that

$$\delta_k^{(1)} E[\Phi] = F_{\delta k} + \text{c.c.} = 0$$

- Since the variation δ is orthogonal on all of the orbitals ($\langle \delta | \varphi_m \rangle = 0 \; \forall \; m$), it follows that $F_{\delta k} = 0$ if

$$\hat{F} \varphi_k = \sum_m \varphi_m \lambda_{mk} \; \forall \; k$$

- These are the general Hartree–Fock equations. The complex conjucate in the upper equation vanishes if and only if $F_{\delta k} = 0$.

- The λ_{km} form a hermitean matrix because $\hat{F}$ is hermitean ($\lambda_{km} = \lambda_{mk}^*$).

- We can linearly transform the MOs such that $\boldsymbol{\lambda}$ becomes the diagonal matrix $\boldsymbol{\varepsilon}$. We then obtain the canonical Hartree–Fock equations.

The canonical Hartree–Fock equations

- We can write the Hartree–Fock equations with a diagonal matrix $\boldsymbol{\lambda}$, which we denote as ε. To see that this is possible, we write the MOs as

$$\varphi_k = \sum_j \tilde{\varphi}_j U_{jk} \quad \text{with a unitary matrix} \quad \mathbf{U}^\dagger \mathbf{U} = \mathbf{U}\mathbf{U}^\dagger = \mathbf{1}$$
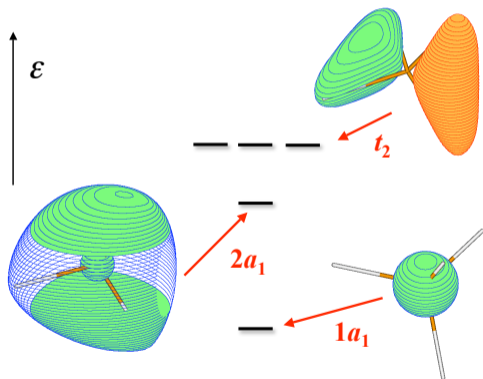
- It then follows that

$$
\begin{aligned}
\hat{F}\varphi_k &= \sum_j \hat{F}\tilde{\varphi}_j U_{jk} = \sum_i \sum_j \tilde{\varphi}_i \tilde{\lambda}_{ij} U_{jk} \\
&= \sum_i \sum_j \sum_m \varphi_m U_{mi}^\dagger \tilde{\lambda}_{ij} U_{jk} = \sum_m \varphi_m \lambda_{mk}
\end{aligned}
$$

Thus, $\boldsymbol{\lambda} = \mathbf{U}^\dagger \tilde{\boldsymbol{\lambda}} \mathbf{U}$, and the unitary matrix $\mathbf{U}$ can be chosen such that $\boldsymbol{\lambda}$ is diagonal, that is, $\lambda_{mk} = \varepsilon_k \delta_{mk}$.

Canonical Hartree–Fock orbitals

- The canonical Hartree–Fock equations read: $\hat{F}\varphi_k = \varepsilon_k \varphi_k$

- By choosing the orbitals such that $\boldsymbol{\lambda}$ is diagonal, we obtain orbital energies ε_k as eigenvalues of the Fock operator.

- Note that canonical orbitals may look different from what you may have expected. The figure shows canonical MOs of methane, for example.

Localised Hartree–Fock orbitals

There are infinitely many Hartree–Fock orbitals that solve the general Hartree–Fock equations and give the same Slater determinant. The canonical MOs are one special choice (with arbitrariness only among degenerate MOs). There are methods to select MOs that are as much as possible localised in space:

- Foster–Boys localisation: the distances between orbital charge centroids are maximised.

- Edmiston-Ruedenberg localisation: the sum of orbital self-repulsion terms is maximised.

- Pipek-Mezey localisation: the number of atom centres spanned by the MOs is minimized. The orbitals are delocalised over as few atoms as possible.

The HF method is invariant with respect to transformations of the MOs. It is very important that post-HF methods are also invariant.

The Hartree–Fock energy

- Once we have determined the canonical MOs by solving the canonical HF equations, we can write the HF energy in terms of orbital energies,

$$
\begin{aligned}
F_{pq} &= h_{pq} + J_{pq} - K_{pq} = h_{pq} + \sum_i \langle ip || iq \rangle \quad \Rightarrow \\
E_{\mathrm{HF}} &= \langle \Phi | \hat{H} | \Phi \rangle = V_{nn} + \sum_i h_{ii} + \tfrac{1}{2} \sum_{i,j} \langle ij || ij \rangle \\
&= V_{nn} + \sum_i F_{ii} - \tfrac{1}{2} \sum_{i,j} \langle ij || ij \rangle = V_{nn} + \sum_i \varepsilon_i - \tfrac{1}{2} \sum_{i,j} \langle ij || ij \rangle
\end{aligned}
$$

- The HF energy is *not equal* to the sum of the orbital energies!
(This is often assumed in semi-empirical theories.)

- The negative orbital energies approximate ionisation potentials (Koopmans' theorem).

Koopmans' theorem

- To describe the system with $(n-1)$ electrons, we simply remove one orbital φ_n from the original set, assuming all the other orbitals to remain unchanged.

- Hence, we neglect orbital-relaxation effects (as well as correlation effects).

- For the energies E_{HF}^n and E_{HF}^{n-1} , we have

$$E_{\mathrm{HF}}^{n-1} \;=\; V_{nn} + \sum_{i=1}^{n-1} h_{ii} + \tfrac{1}{2} \sum_{i,j=1}^{n-1} \langle ij||ij \rangle$$

$$E_{\mathrm{HF}}^{n} \;=\; E_{\mathrm{HF}}^{n-1} + h_{nn} + \tfrac{1}{2} \sum_{i}^{n-1} \langle in||in \rangle + \tfrac{1}{2} \sum_{j=1}^{n-1} \langle nj||nj \rangle + \tfrac{1}{2} \langle nn||nn \rangle$$

- Since $\langle nn||nn \rangle = 0$, we find

$$E_{\mathrm{HF}}^{n-1} - E_{\mathrm{HF}}^{n} = -h_{nn} - \sum_{i}^{n} \langle in||in \rangle = -\varepsilon_n$$

Koopmans' theorem

The table shows the computed first ionisation potential (IP) of the Na atom. All values in eV. The experimental value is 5.14 eV.

Theory	$-\varepsilon_{\mathrm{HOMO}}(\mathrm{Na})$	ΔE	$-\varepsilon_{\mathrm{average}}$
Hartree–Fock	4.96	4.95	–
LDA	3.08	5.37	5.05
BLYP	2.90	5.36	5.32
B3LYP	3.40	5.35	5.27

- $\varepsilon_{\mathrm{HOMO}}(\mathrm{Na})$ is the orbital energy of the highest occupied MO.

- ΔE is the difference between the energies of Na and Na^+.

- $\varepsilon_{\mathrm{average}} = \frac{1}{2}\left\{\varepsilon_{\mathrm{HOMO}}(\mathrm{Na}) + \varepsilon_{\mathrm{LUMO}}(\mathrm{Na}^+)\right\}$, the average of the HOMO of Na and the LUMO (lowest unoccupied MO) of Na^+.

- For Na, the orbital-relaxation effect is small.

Frontier orbitals

- So far, we have only considered $\hat{F}\varphi_k = \varepsilon_k \varphi_k$ or $\hat{F}\varphi_k = \sum_m \varphi_m \lambda_{mk}$, where the set $\{\varphi_k\}$ forms the Slater determinant. These are occupied MOs, for which we use the indices $i, j, k, \ldots$.

- The orbital φ_k with the highest (= least negative) eigenvalue is the highest occupied molecular orbital, HOMO.

- The Fock operator $\hat{F}$, however, has many more eigenfunctions. The HF solutions form a complete set of (square integrable) one-electron functions,

$$\hat{F}\varphi_a = \varepsilon_a \varphi_a \quad \text{or} \quad \hat{F}\varphi_a = \sum_c \varphi_c \lambda_{ca}, \quad \varphi_c \notin \{\varphi_k\}$$

- The orbitals with index $a, b, c, \ldots$ are denoted unoccupied or virtual orbitals. The orbital φ_a with the lowest eigenvalue is the lowest unoccupied molecular orbital, LUMO.

- HOMO and LUMO are the frontier orbitals.

The LUMO of Hartree–Fock theory

- The LUMO is the lowest unoccupied MO. It has no meaning at all and cannot be used to estimate the electron affinity (EA).

- But we can consider the HOMO of the anion to estimate the EA of the neutral.

- Consider the Li atom. Its experimentally determined electron affinity amounts to EA(exp) = 0.62 eV.

Theory	$-\varepsilon_{\mathrm{HOMO}}(\mathrm{Li}^-)$	ΔE
Hartree–Fock	0.40	–0.12
CCSD(T)/WMR		0.62

- The HOMO of Li$^-$ is negative, and hence, 4 electrons are bound at the Hartree–Fock level, but the Hartree–Fock energy of Li$^-$ is 0.12 eV *higher* than that of neutral Li.

- WMR = Widmark–Malmqvist–Roos $7s6p4d3f$ ANO basis.
  (In this basis, the HF results is also -0.12 eV.)

Removing two electrons / excitation energies

- If we were to remove two electrons from the orbitals φ_k and φ_l, then the energy change will not simply be the sum of the orbital energies. Rather,

$$E_{\mathrm{HF}}^{n-2} - E_{\mathrm{HF}}^{n} = -\varepsilon_k - \varepsilon_l + \langle kl || kl \rangle$$

- Similarly, if we were to compute an "excitation energy" by removing an electron from an occupied orbital φ_i and adding it to a virtual orbital φ_a, we would obtain:

$$\Delta E_{\mathrm{HF}}^{i \to a} = E_i^a - E_0 = \varepsilon_a - \varepsilon_i - \langle ia || ia \rangle$$

- Remember that the total Hartree–Fock energy is not the sum of the orbital energies.