The Hartree-Fock Method

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Overview

Motivation

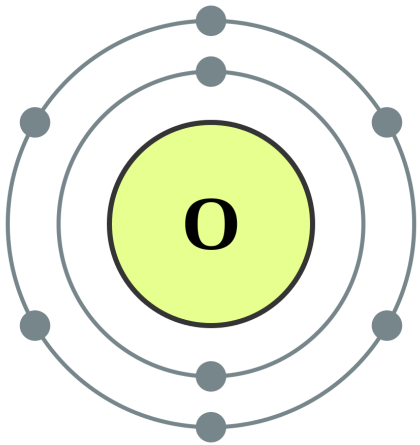
- The time-independent Schrödinger equation is defined as

$$\hat{H}\Psi(\mathbf{x}) = E\Psi(\mathbf{x}) \quad , \tag{1}$$

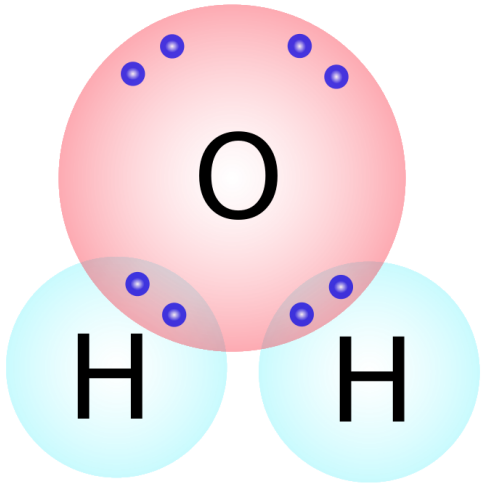
  where $\hat{H}$ ist the Hamiltonian operator and E is the energy of the state Ψ
- Find an approximate solution of the time-independent Schrödinger equation for a many-body system

Examples of Many-Body Systems

- Multi-electron atoms
- Molecules



(a) Oxygen



(b) Water molecule

The Molecular Hamiltonian Operator

$$\hat{H} = \overbrace{\sum_{i=1}^{K\ \text{nuclei}} -\frac{\hbar^2}{2m_i}\nabla^2_{\mathbf{r}_i} + \sum_{j=1}^{N\ \text{electrons}} -\frac{\hbar^2}{2m_i}\nabla^2_{\mathbf{r}_j}}^{\text{Kinetic energy (nucl. and el.)}} + \overbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{k=1}^{N}\sum_{l>k}^{N}\frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l|}}^{\text{Coulomb repulsion (el.-el.)}}$$
$$\underbrace{-\frac{1}{4\pi\epsilon_0}\sum_{m=1}^{K}\sum_{n=1}^{N}\frac{Z_m e^2}{|\mathbf{r}_n - \mathbf{R}_m|}}_{\text{Coulomb attraction (el.-nucl.)}} + \underbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{o=1}^{K}\sum_{p>0}^{K}\frac{Z_o Z_p e^2}{|\mathbf{R}_o - \mathbf{R}_k|}}_{\text{Coulomb repulsion (nucl.-nucl.)}} \qquad (2)$$

Born-Oppenheimer Approximation

- Nuclei of atoms are often much heavier than electrons
- Consider nuclei as stationary to calculate properties of the electrons
- Hamiltonian operator for electrons:

$$\hat{H}_{\text{el}} = \overbrace{\sum_{j=1}^{N \text{ electrons}} -\frac{\hbar^2}{2m_i}\nabla^2_{\mathbf{r}_j}}^{\text{Kinetic energy (el.)}} + \overbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{k=1}^{N}\sum_{l>k}^{N}\frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l|}}^{\text{Coulomb repulsion (el.-el.)}} \underbrace{-\frac{1}{4\pi\epsilon_0}\sum_{m=1}^{K}\sum_{n=1}^{N}\frac{Z_m e^2}{|\mathbf{r}_n - \mathbf{R}_m|}}_{\text{Coulomb attraction (el.-nucl.)}} \tag{3}$$

Hilbert Space

- Single-body quantum system is described by a Hilbert space $\mathcal{H}$ of dimension $\dim \mathcal{H} = d$
- N distinguishable particles are described by tensor product of N single-body Hilbert spaces

$$\mathcal{H}^{(N)} \equiv \mathcal{H}^{\otimes N} = \bigotimes_{i=1}^{N} \mathcal{H} \tag{4}$$

with

$$\dim \mathcal{H}^{(N)} = d^N \tag{5}$$

Complexity of the Hilbert Space

- d^N basis functions are needed to span the Hilbert space $H^{(N)}$
- Exponential scaling of the Hilbert space dimension with number of particles is a big challenge
  - Single fermion has a Hilbert space $\mathcal{H} = \mathbb{C}^2$ with $\dim \mathcal{H} = 2$
  - N fermions have Hilbert space $\mathcal{H}^{(N)} = \mathbb{C}^{2^N}$ with $\dim \mathcal{H}^{(N)} = 2^N$
  - Basis for $N = 30$ fermions is already of size 2^{30}, i.e., over one billion basis functions

Many-Fermion System I

- Use Hartree product ansatz for many-particle wave function:

$$\psi\left(\mathbf{r}_1, \ldots, \mathbf{r}_N\right) \approx \prod_{i=1}^{N} \phi_i(\mathbf{r}_i) \quad , \tag{6}$$

  where ϕ_i is a single-particle wave function

- **Problem**: Hartree product does not take into account antisymmetric properties of fermions, i.e.,

$$\hat{P}_{12}\,\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_2, \mathbf{r}_1) = \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1) \neq -\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) \quad ,$$

  where $\hat{P}_{12}$ is the exchange operator

Many-Fermion System II

- **Solution**: Fermionic wave function has to be antisymmetric under particle exchange, thus the antisymmetrized wave function is defined as

$$\Psi^{(A)} = \frac{1}{\sqrt{N!}} \sum_{p} \mathrm{sgn}(p)\, \psi\left(\mathbf{r}_{p(1)}, \ldots, \mathbf{r}_{p(N)}\right) \tag{7}$$

  - $1/\sqrt{N!}$ is the normalization factor
  - Sum goes over all permutations p of N particles
  - $\mathrm{sgn}(p) = +1$ if p represents an even number of permutations, else $\mathrm{sgn}(p) = -1$

Slater Determinant

- The many-fermion wave function in Eq. 7 can be written as a Slater determinant:

$$\Psi^{(A)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix} \tag{8}$$

- The set of antisymmetrized Slater determinants forms the basis of the many-particle Hilbert space $H^{(N)}$
- Example: For a two-electron system we would have

$$\Psi^{(A)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left[\phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2) - \phi_1(\mathbf{r}_2)\phi_2(\mathbf{r}_1)\right] \tag{9}$$

Restrictions of the First Quantization

- Cumbersome to work with appropriately symmetrized many-body wave functions
- It is restricted to exactly N particles
  - Quantum field theory: systems with variable particle numbers
  - Solid state physics: infinite number of electrons

Fock Space

- $N = 0, 1, \ldots, \infty$ *indistinguishable* particles are described by the Fock space which is defined as

$$F(\mathcal{H}) = \bigoplus_{N=0}^{\infty} \mathcal{S}_{\pm} \mathcal{H}^{\otimes N} \tag{10}$$

  - $\mathcal{S}_+$ is the symmetrization operator used for bosons
  - $\mathcal{S}_-$ is the anti-symmetrization operator used for fermions

The Occupation Number Basis I

- Let $\{|\phi_1\rangle, \ldots, |\phi_L\rangle\}$ be the basis of the single-particle Hilbert space $\mathcal{H}$
- The Fock space basis consists of states (called Fock states) constructed by specifying the number of particles N_α occupying the single-particle state $|\phi_\alpha\rangle$, i.e.,

$$|N_1, N_2, \ldots, N_L\rangle \tag{11}$$

- For fermions: $N_\alpha \in \{0, 1\}$ (Pauli exclusion principle)

The Occupation Number Basis II

- Fock space is the space of all occupation number states for all particle numbers N

N **particles**	**Fermionic basis states**
0	$\|0,0,0,\ldots\rangle$
1	$\|1,0,0,\ldots\rangle, \|0,1,0,\ldots\rangle, \|0,0,1,\ldots\rangle, \ldots$
2	$\|1,1,0,\ldots\rangle, \|0,1,1,\ldots\rangle, \|1,0,1,\ldots\rangle, \ldots$
$\ldots$	$\ldots$

Fermion Creation Operator $\hat{a}_\alpha^\dagger$ I

- In Fock space, the fermion creation operator $\hat{a}_\alpha^\dagger$ for the single-particle state $|\phi\rangle_\alpha$ is introduced
- $\hat{a}_\alpha^\dagger$ increases the occupation number of N_α by 1 if $N_\alpha = 0$, e.g.,

$$\hat{a}_2^\dagger |1, 0, 0, \ldots\rangle = |1, 1, 0, \ldots\rangle \tag{12}$$

- Fermion creation in a single-particle state that is already occupied destroys the state, e.g.,

$$\hat{a}_1^\dagger |1, 1, 0, \ldots\rangle = 0 \tag{13}$$

Fermion Creation Operator $\hat{a}^\dagger_\alpha$ II

- Fermion creation operators have to anticommute, meaning

$$\left\{\hat{a}^\dagger_\alpha, \hat{a}^\dagger_\beta\right\} = 0 \tag{14}$$

- Eq. 14 is needed, since Fock states are antisymmetric under interchange of pairs of fermions, i.e.,

$$\hat{a}^\dagger_\alpha \hat{a}^\dagger_\beta \left|0\right\rangle = -\hat{a}^\dagger_\beta \hat{a}^\dagger_\alpha \left|0\right\rangle \tag{15}$$

- Further, Eq. 14 ensures that a state is destroyed if one tries to create a fermion in an already occupied state, since

$$\left(\hat{a}^\dagger_\alpha\right)^2 = 0 \tag{16}$$

Fock Basis in Second Quantization

- The Fock state $|N_1, N_2, \ldots, N_L\rangle$ in the occupation number basis can be expressed in terms of creation operators:

$$|N_1, N_2, \ldots, N_L\rangle = \prod_{i=1}^{L} \left(a_i^\dagger\right)^{N_i}$$
$$= \left(a_1^\dagger\right)^{N_1} \left(a_2^\dagger\right)^{N_2} \cdots \left(a_L^\dagger\right)^{N_L} |0\rangle \quad (17)$$

- Fermion creation operators anticommute, thus ordering of the operators matters
- The normal ordering that is used from now on is defined by Eq. 17

Fermion Annihilation Operator $\hat{a}_\alpha$

- Fermion annihilation operator $\hat{a}_\alpha$ decreases the occupation number of N_α by 1 if $N_\alpha = 1$, e.g.,

$$\hat{a}_1 \left|1, 0, 0, \ldots\right\rangle = \left|0, 0, 0, \ldots\right\rangle \tag{18}$$

- Fermion annihilation in a single-particle state that is not occupied destroys the state, e.g.,

$$\hat{a}_2 \left|0, 0, 0, \ldots\right\rangle = 0 \tag{19}$$

- Fermion annihilation operators anticommute, i.e.,

$$\{\hat{a}_\alpha, \hat{a}_\beta\} = 0 \tag{20}$$

Definition of $\hat{a}_\alpha^\dagger$ and $\hat{a}_\alpha$ I

$$\hat{a}_\alpha^\dagger \left|N_1, N_2, \ldots, N_\alpha, \ldots\right\rangle = \delta_{N_\alpha 0}(-1)^{S_\alpha} \left|N_1, N_2, \ldots, N_\alpha + 1, \ldots\right\rangle \tag{21}$$

$$\hat{a}_\alpha \left|N_1, N_2, \ldots, N_\alpha, \ldots\right\rangle = \delta_{N_\alpha 1}(-1)^{S_\alpha} \left|N_1, N_2, \ldots, N_\alpha - 1, \ldots\right\rangle \tag{22}$$

where

$$S_\alpha \equiv \sum_{\gamma<\alpha} N_\gamma \tag{23}$$

and $\delta_{ij} = 1$ if $i = j$ and 0 otherwise

Definition of $\hat{a}_\alpha^\dagger$ and $\hat{a}_\alpha$ II

From Eqs. 21 and 22 it follows that the antisymmetric property of fermions is fulfilled, since

$$\hat{a}_\alpha^\dagger \hat{a}_\beta = -\hat{a}_\beta \hat{a}_\alpha^\dagger \qquad (\alpha \neq \beta) \tag{24}$$

One-Particle Operators I

- One-particle operator $\hat{V}^{(1)}$ consists of a sum of N identical operators $\hat{V}_i$ acting only on the Hilbert space of the i-th electron

$$\hat{V}^{(1)} = \sum_{i=1}^{N} \hat{V}_i \tag{25}$$

- Example: the kinetic energy operator defined as

$$\hat{T} = \sum_{i=1}^{N} \frac{\hat{p}_i^2}{2m_i} \tag{26}$$

One-Particle Operators II

- $\hat{V}_i$ operating on a one-electron wave function $\phi_\alpha(\mathbf{r}_i, s_i)$ it produces a superposition of one-electron wave functions

$$\hat{V}_i \phi_\alpha(\mathbf{r}_i, s_i) = \sum_\beta V_{\beta\alpha} \phi_\beta(\mathbf{r}_i, \mathbf{s}_i) \tag{27}$$

with the amplitudes

$$V_{\beta\alpha} \equiv \langle i, \beta | \hat{V}_i | i, \alpha \rangle \tag{28}$$

One-Particle Operators III

- Applying $\hat{V}^{(1)}$ on a Fock state a superposition of states is generated

$$\hat{V}^{(1)} \left|\alpha_1, \ldots, \alpha_i, \ldots, \alpha_L\right\rangle \tag{29}$$

$$= \sum_{\beta} \sum_{i=1}^{L} V_{\beta\alpha_i} \left|\alpha_1, \ldots, \alpha_i \rightarrow \beta, \ldots, \alpha_L\right\rangle \tag{30}$$

- $\left|\alpha_1, \ldots, \alpha_i \rightarrow \beta, \ldots, \alpha_L\right\rangle$ denotes the state obtained from $\left|\alpha_1, \ldots, \alpha_i, \ldots, \alpha_L\right\rangle$ upon replacing ϕ_{α_i} by ϕ_β

$$\left|\alpha_1, \ldots, \alpha_i \rightarrow \beta, \ldots, \alpha_L\right\rangle = \hat{a}_\beta^\dagger \hat{a}_{\alpha_i} \left|\alpha_1, \ldots, \alpha_i, \ldots, \alpha_L\right\rangle \tag{31}$$

One-Particle Operators IV

- The one-particle operator $\hat{V}^{(1)}$ can now be expressed as

$$\hat{V}^{(1)} = \sum_{\alpha,\beta} V_{\beta\alpha} \hat{a}^{\dagger}_{\beta} \hat{a}_{\alpha} \tag{32}$$

Two-Particle Operators I

- Two-particle operator $\hat{V}^{(2)}$ consists of a sum of N identical operators $\hat{V}_{ij}$ acting on the Hilbert spaces of two electrons

$$\hat{V}^{(2)} = \frac{1}{2}\sum_{i\neq j}^{N} \hat{V}_{ij} \tag{33}$$

- Example: Coulomb interaction term

$$\frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{34}$$

Two-Particle Operators II

- Analogous to the derivation shown for the one-particle operator, one obtains for the two-particle operator $\hat{V}^{(2)}$

$$\hat{V}^{(2)} = \frac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} V_{\alpha,\beta,\gamma,\delta} \hat{a}^{\dagger}_{\alpha} \hat{a}^{\dagger}_{\beta} \hat{a}_{\gamma} \hat{a}_{\delta} \tag{35}$$

with the amplitudes

$$V_{\gamma\delta\alpha\beta} \equiv \left(\langle i, \gamma | \langle j, \delta | \right) \hat{V}_{ij} \left(| j, \alpha \rangle | i, \beta \rangle \right) \tag{36}$$

Hamilton Operator in Second Quantized Notation I

- Use basis set of L orbital wave functions $\{f_i\}$
- The matrix elements of $\hat{H}_{\text{el}}$ (Eq. 3) are defined as

$$t_{ij} = \int \mathrm{d}^3\mathbf{r} f_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}_i) \right) f_j(\mathbf{r}) \tag{37}$$

$$V_{ijkl} = e^2 \int \mathrm{d}^3\mathbf{r} \int \mathrm{d}^3\mathbf{r}' f_i^*(\mathbf{r}) f_j(\mathbf{r}) \frac{1}{|\mathbf{r}-\mathbf{r}'|} f_k^*(\mathbf{r}') f_l(\mathbf{r}') \tag{38}$$

where t_{ij} is a one-particle and V_{ijkl} a two-particle operator, and

$$V(\mathbf{r}) = -\frac{1}{4\pi\epsilon_0} \sum_{m=1}^{K} \frac{Z_m e^2}{|\mathbf{r}-\mathbf{R}_m|} \tag{39}$$

Hamilton Operator in Second Quantized Notation II

- $\hat{H}_{\text{el}}$ can now be written in second quantized notation as

$$\hat{H}_{\text{el}} = \sum_{ij\sigma} t_{ij}\, \hat{a}^{\dagger}_{i\sigma}\, \hat{a}_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl}\, \hat{a}^{\dagger}_{i\sigma}\, \hat{a}^{\dagger}_{k\sigma'}\, \hat{a}_{i\sigma'}\, \hat{a}_{j\sigma} \tag{40}$$

The Hartree-Fock Approximation

- Approximation is based on the assumption of independent electrons
- N-fermion ground state wave function is represented as a single Slater determinant

$$\Psi^{(\mathrm{HF})} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1, \sigma_1) & \dots & \phi_N(\mathbf{r}_1, \sigma_1) \\ \vdots & & \vdots \\ \phi_1(\mathbf{r}_N, \sigma_N) & \dots & \phi_N(\mathbf{r}_N, \sigma_N) \end{vmatrix} \tag{41}$$

The Hartree-Fock Equations I

- Closed-shell conditions are assumed, i.e., each orbital is occupied by both an electron with spin $\uparrow$ and spin $\downarrow$
- $\Psi^{(\mathrm{HF})}$ (Eq. 41) in second quantized form:

$$|\Psi\rangle^{(\mathrm{HF})} = \prod_{\mu,\sigma} c^{\dagger}_{\mu\sigma} |0\rangle \tag{42}$$

where $c^{\dagger}_{\mu\sigma}$ is orthogonal and creates an electron in the orbital $\phi_{\mu}(\mathbf{r}, \sigma)$

The Hartree-Fock Equations II

- $c^{\dagger}_{\mu\sigma}$ is expanded in terms of creation operators $\hat{a}^{\dagger}_{n\sigma}$ of our finite basis set:

$$c^{\dagger}_{\mu\sigma} = \sum_{n=1}^{L} d_{\mu n} \hat{a}^{\dagger}_{n\sigma} \tag{43}$$

The Hartree-Fock Equations II

- Bond-order matrix is introduced:

$$P_{ij} = \sum_{\sigma} \left\langle \Psi^{(\mathsf{HF})} \right| \hat{a}^{\dagger}_{i\sigma} \hat{a}_{j\sigma} \left| \Psi^{(\mathsf{HF})} \right\rangle = 2 \sum_{\nu} d^{*}_{\nu i} d_{\nu j} \tag{44}$$

- The kinetic term of $\hat{H}_{\mathsf{el}}$ is simplified to

$$\sum_{ij\sigma} t_{ij} \hat{a}^{\dagger}_{i\sigma} \hat{a}_{j\sigma} = \sum_{ij} P_{ij} t_{ij} \tag{45}$$

The Hartree-Fock Equations III

- The interaction term becomes

$$\left\langle \Psi^{(\mathrm{HF})} \right| a_{i\sigma}^{\dagger} a_{k\sigma'}^{\dagger} \hat{a}_{l\sigma'} \hat{a}_{j\sigma} \left| \Psi^{(\mathrm{HF})} \right\rangle = \begin{cases} P_{ij}P_{kl} - P_{il}P_{kj}, & \sigma = \sigma' \\ P_{ij}P_{kl}, & \sigma \neq \sigma' \end{cases} \tag{46}$$

- Thus, the interaction term of $\hat{H}_{\mathrm{el}}$ simplfies to

$$\frac{1}{2} \sum_{ijkl} \left(V_{ijkl} - \frac{1}{2} V_{ilkj} \right) P_{ij} P_{kl} \tag{47}$$

The Hartree-Fock Equations IV

- Combining Eqs. 45 and 47 leads to the energy term

$$E^{(\mathsf{HF})} = \left\langle \Psi^{(\mathsf{HF})} \right| H \left| ^{(\mathsf{HF})} \right\rangle$$
$$= \sum_{ij} P_{ij} t_{ij} + \frac{1}{2} \sum_{ijkl} \left(V_{ijkl} - \frac{1}{2} V_{ilkj} \right) P_{ij} P_{kl} \quad (48)$$

The Hartree-Fock Equations V

- Minimize $E^{(\mathrm{HF})}$ under the condition that the states $|\phi\rangle_\mu$ are normalized:

$$1 = \langle \phi_\mu | \, \phi_\mu \rangle = \sum_{i,j} d^*_{\mu i} d_{\mu j} S_{ij} \tag{49}$$

with the overlap matrix $\underline{\mathbf{S}}$ defined as

$$S_{ij} = \int \mathrm{d}^3\mathbf{r} f_i^*(\mathbf{r}) f_j(\mathbf{r}) \, ap \tag{50}$$

  - $\underline{\mathbf{S}}$ is the identity matrix for an orthonormal basis set

The Hartree-Fock Equations VI

- Introduce Lagrange multipliers to enforce the constraint we have to minimize

$$\sum_{ij} P_{ij} t_{ij} + \frac{1}{2} \sum_{ijkl} \left(V_{ijkl} - \frac{1}{2} V_{ilkj} \right) P_{ij} P_{kl} - \sum_{\mu} \epsilon_{\mu} \sum_{i,j} d^{*}_{\mu i} d_{\mu j} S_{ij} \tag{51}$$

The Hartree-Fock Equations VII

- Set the derivative with respect to $d_{\mu i}$ to zero to get the Hartree-Fock equations for a finite basis set:

$$\sum_{j=1}^{L}(f_{ij} - \epsilon_\mu S_{ij})\, d_{\mu j} = 0 \tag{52}$$

with

$$f_{ij} = t_{ij} + \sum_{kl}\left(V_{ijkl} - \frac{1}{2} V_{ilkj} \right) P_{kl} \tag{53}$$

The Hartree-Fock Equations VIII

- Eq. 52 is a nonlinear generalized eigenvalue problem of the form

$$\underline{\mathbf{F}}[\mathbf{x}]\mathbf{x} = \lambda \underline{\mathbf{S}}\mathbf{x} \tag{54}$$

  where $\underline{\mathbf{F}}$ is the potential matrix and $\underline{\mathbf{S}}$ is the overlap matrix
- Eq. 54 can only be solved iteratively until convergence to a fixed point is achieved, since $\underline{\mathbf{F}}$ depends on the solution $\mathbf{x}$

The Hartree-Fock Equations IX

- The ground state energy E^0 can be found using

$$E_0 = \sum_{\nu=1}^{N} \epsilon_\nu - \frac{1}{2} \sum_{ijkl} \left(V_{ijkl} - \frac{1}{2} V_{ilkj} \right) P_{ij} P_{kl} \tag{55}$$

  - The second term in Eq. 55 has to be subtracted, since the two-electron integrals are counted double

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