perturbative analysis pt. 2

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(Löwdin partitioning)

$\Phi \equiv$

$\Phi \equiv$ row vector of $\mathcal{F}_n$ determinants

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$=$

$$\Phi \equiv \text{row vector of } \mathcal{F}_n \text{ determinants}$$

$$= [\Phi, \Phi_1, \ldots, \Phi_n]$$

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$\Rightarrow$

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$$\Rightarrow |\Phi\rangle\langle\Phi| = 1_n$$

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$$\Rightarrow |\Phi\rangle\langle\Phi| = 1_n$$

$$\langle\Phi|H|\Phi\rangle\langle\Phi|\Psi\rangle = E\langle\Phi|\Psi\rangle$$

$\Phi \equiv$ row vector of $\mathcal{F}_n$ determinants

$= [\Phi, \Phi_1, \ldots, \Phi_n]$

$\Rightarrow |\Phi\rangle\langle\Phi| = 1_n$

$$\underbrace{\langle\Phi|H|\Phi\rangle}_{\mathbb{H}}\langle\Phi|\Psi\rangle = E\langle\Phi|\Psi\rangle$$

$\Phi \equiv$ row vector of $\mathcal{F}_n$ determinants

$$= [\Phi, \Phi_1, \ldots, \Phi_n]$$

$$\Rightarrow |\Phi\rangle\langle\Phi| = 1_n$$

$$\underbrace{\langle\Phi|H|\Phi\rangle}_{\downarrow \atop \mathbb{H}}\underbrace{\langle\Phi|\Psi\rangle}_{\downarrow \atop \mathbb{c}} = E\underbrace{\langle\Phi|\Psi\rangle}_{\downarrow \atop \mathbb{c}}$$

Löwdin partitioning:

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Φ

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$$\Phi =$$

Löwdin partitioning:

$$\Phi = \left[\Phi \;\; \Phi_1 \cdots \Phi_m \;\; \Phi_{m+1} \cdots \Phi_n \right]$$

Löwdin partitioning:

$$\Phi = \left[\underbrace{\Phi \;\; \Phi_1 \cdots \Phi_m}_{\Phi_i} \; \Phi_{m+1} \cdots \Phi_n \right]$$

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$$\Phi = [\underbrace{\Phi \quad \Phi_1 \cdots \Phi_m}_{\Phi_i} \; \underbrace{\Phi_{m+1} \cdots \Phi_n}_{\Phi_e}]$$

Löwdin partitioning:

$$\Phi = [\,\underbrace{\Phi \;\; \Phi_1 \cdots \Phi_m}_{\Phi_i} \; \underbrace{\Phi_{m+1} \cdots \Phi_n}_{\Phi_e}\,]$$

$$\mathbb{1}_{|\mathcal{F}_a|}$$

Löwdin partitioning:

$$\Phi = [\underbrace{\Phi \quad \Phi_1 \cdots \Phi_m}_{\Phi_i} \; \underbrace{\Phi_{m+1} \cdots \Phi_n}_{\Phi_e}]$$

$$\mathbb{1}_{|\mathcal{F}_a|} = \mathbb{1}_i + \mathbb{1}_e$$

Löwdin partitioning:

$$\Phi = \Big[\, \underbrace{\Phi \quad \Phi_1 \cdots \Phi_m}_{\Phi_i} \; \underbrace{\Phi_{m+1} \cdots \Phi_n}_{\Phi_e} \,\Big]$$

$$\mathbb{1}_{|\mathcal{F}_a|} = \mathbb{1}_i + \mathbb{1}_e$$

$$\downarrow$$

$$\begin{bmatrix} \mathbb{1} & 0 \\ 0 & 0 \end{bmatrix}$$

Löwdin partitioning:

$$\Phi = [\underbrace{\Phi \quad \Phi_1 \cdots \Phi_m}_{\Phi_i} \; \underbrace{\Phi_{m+1} \cdots \Phi_n}_{\Phi_e}]$$

$$\mathbb{1}_{|\mathcal{F}_a|} = \underset{\begin{bmatrix} \mathbb{1} & 0 \\ 0 & 0 \end{bmatrix}}{\underset{\downarrow}{\mathbb{1}_i}} + \underset{\begin{bmatrix} 0 & 0 \\ 0 & \mathbb{1} \end{bmatrix}}{\underset{\downarrow}{\mathbb{1}_e}}$$

H

$\mathbb{H} =$

$$\mathbb{H} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{H}$$

$$\mathbb{H} = (\mathbb{1}_i + \mathbb{1}_e)\, \mathbb{H}\, (\mathbb{1}_i + \mathbb{1}_e)$$

$$
\begin{aligned}
\mathbb{H} &= (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{H}\,(\mathbb{1}_i + \mathbb{1}_e) \\
&= \mathbb{H}_{ii} + \mathbb{H}_{ie} + \mathbb{H}_{ei} + \mathbb{H}_{ee}
\end{aligned}
$$

$$\mathbb{H} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{H}\,(\mathbb{1}_i + \mathbb{1}_e)$$
$$= \mathbb{H}_{ii} + \mathbb{H}_{ie} + \mathbb{H}_{ei} + \mathbb{H}_{ee}$$

$\mathbb{G}$

$$\mathbb{H} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{H}\,(\mathbb{1}_i + \mathbb{1}_e)$$
$$= \mathbb{H}_{ii} + \mathbb{H}_{ie} + \mathbb{H}_{ei} + \mathbb{H}_{ee}$$

$$\mathbb{G} =$$

$$\mathbb{H} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{H}\,(\mathbb{1}_i + \mathbb{1}_e)$$
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$$\mathbb{G} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{G}$$

$$\mathbb{H} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{H}\,(\mathbb{1}_i + \mathbb{1}_e)$$

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$$\mathbb{G} = (\mathbb{1}_i + \mathbb{1}_e)\,\mathbb{G}$$

$$= \mathbb{G}_i + \mathbb{G}_e$$

External space resolvent:

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$$R_{ee}$$

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$$R_{ee} \equiv$$

External space resolvent:

$$R_{ee} \equiv (E-H)^{-1}\Big|_{e}$$

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$$R_{ee} \equiv (E-H)^{-1}\big|_e$$

$$= |\Phi_e\rangle\langle\Phi_e|E-H|\Phi_e\rangle^{-1}\langle\Phi_e|$$

External space resolvent:

$$R_{ee} \equiv (E-H)^{-1}\big|_e$$

$$= |\Phi_e\rangle \underbrace{\langle \Phi_e | E - H | \Phi_e \rangle^{-1}}_{\mathbb{R}_{ee}} \langle \Phi_e |$$

$$\mathbb{R}_{ce}(E - \mathbb{H})$$

$$\mathbb{R}_{ce}(E - \mathbb{H}) =$$

$$\mathbb{R}_{ce}(E - \mathbb{H}) = \mathbb{R}_{ce}(E - \mathbb{H})$$

$$\mathbb{R}_{ce}(E - \mathbb{H}) = \mathbb{R}_{ce}(E - \mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$\mathbb{R}_{ce}(E - \mathbb{H}) = \mathbb{R}_{ce}(E - \mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$=$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\,\mathbb{H}_{ei}$$

$$
\begin{aligned}
\mathbb{R}_{ee}(E-\mathbb{H}) &= \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e) \\
&= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \mathbb{R}_{ee}(E-\mathbb{H})_{ee}
\end{aligned}
$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{0} = \mathbb{R}_{ee}(E-\mathbb{H})\,\mathbb{G}$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{0} = \mathbb{R}_{ee}(E-\mathbb{H})\,\mathbb{G} = (-\mathbb{R}_{ee}\mathbb{H}_{ei} + \mathbb{1}_e)\,\mathbb{G}$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{0} = \mathbb{R}_{ee}(E-\mathbb{H})\,\mathbb{C} = (-\mathbb{R}_{ee}\mathbb{H}_{ei} + \mathbb{1}_e)\,\mathbb{C}$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei}\mathbb{C}_i + \mathbb{C}_e$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{0} = \mathbb{R}_{ee}(E-\mathbb{H})\,\mathbb{G} = (-\mathbb{R}_{ee}\mathbb{H}_{ei} + \mathbb{1}_e)\,\mathbb{G}$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei}\mathbb{G}_i + \mathbb{G}_e$$

$$\Longrightarrow$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{0} = \mathbb{R}_{ee}(E-\mathbb{H})\,\mathbb{G} = (-\mathbb{R}_{ee}\mathbb{H}_{ei} + \mathbb{1}_e)\,\mathbb{G}$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei}\mathbb{G}_i + \mathbb{G}_e$$

$$\Longrightarrow \mathbb{G}_e$$

$$\mathbb{R}_{ee}(E-\mathbb{H}) = \mathbb{R}_{ee}(E-\mathbb{H})(\mathbb{1}_i + \mathbb{1}_e)$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei} + \cancelto{\mathbb{1}_e}{\mathbb{R}_{ee}(E-\mathbb{H})_{ee}}$$

operate resolvent on Schrödinger eq.:

$$\mathbb{0} = \mathbb{R}_{ee}(E-\mathbb{H})\,\mathbb{C} = (-\mathbb{R}_{ee}\mathbb{H}_{ei} + \mathbb{1}_e)\,\mathbb{C}$$

$$= -\mathbb{R}_{ee}\mathbb{H}_{ei}\mathbb{C}_i + \mathbb{C}_e$$

$$\Longrightarrow \quad \mathbb{C}_e = \mathbb{R}_{ee}\mathbb{H}_{ei}\mathbb{C}_i$$

$E\,c_i$

$$E\,q_i =$$

$$E\,\mathbb{C}_i = \mathbb{1}_i \mathbb{H} \mathbb{C}$$

$$E\,\mathbb{C}_i = \mathbb{1}_i \mathbb{H} \mathbb{C} (\mathbb{1}_i + \mathbb{1}_e)$$

$$E\,\mathbb{C}_i = \mathbb{1}_i\,\mathbb{H}\,\mathbb{C}\,(\mathbb{1}_i + \mathbb{1}_e)$$

$$= \mathbb{H}_{ii}\,\mathbb{C}_i + \mathbb{H}_{ie}\,\mathbb{C}_e$$

$$E\,\mathbb{C}_i = \mathbb{1}_i\,\mathbb{H}\,\mathbb{C}\,(\mathbb{1}_i + \mathbb{1}_e)$$

$$= \mathbb{H}_{ii}\,\mathbb{C}_i + \mathbb{H}_{ie}\,\overset{\mathbb{R}_{ee}\,\mathbb{H}_{ei}\,\mathbb{C}_i}{\cancel{\mathbb{C}_e}}$$

$$
\begin{aligned}
E\,\mathbb{G}_i &= \mathbb{1}_i\,\mathbb{H}\,\mathbb{G}\,(\mathbb{1}_i + \mathbb{1}_e) \\
&= \mathbb{H}_{ii}\,\mathbb{G}_i + \mathbb{H}_{ie}\,\cancelto{\mathbb{R}_{ee}\,\mathbb{H}_{ei}\,\mathbb{G}_i}{\mathbb{G}_e}
\end{aligned}
$$

$\Longrightarrow$

$$
\begin{aligned}
E\,\mathbb{G}_i &= \mathbb{1}_i\,\mathbb{H}\,\mathbb{G}\,(\mathbb{1}_i + \mathbb{1}_e) \\
&= \mathbb{H}_{ii}\,\mathbb{G}_i + \mathbb{H}_{ie}\,\cancelto{\mathbb{R}_{ee}\,\mathbb{H}_{ei}\,\mathbb{G}_i}{\mathbb{G}_e}
\end{aligned}
$$

$$
\Longrightarrow\ (\mathbb{H}_{ii} + \mathbb{H}_{ie}\,\mathbb{R}_{ee}\,\mathbb{H}_{ei})\,\mathbb{G}_i = E\,\mathbb{G}_i
$$

$$E\,\mathbb{C}_i = \mathbb{1}_i\,\mathbb{H}\,\mathbb{C}\,(\mathbb{1}_i + \mathbb{1}_e)$$

$$= \mathbb{H}_{ii}\,\mathbb{C}_i + \mathbb{H}_{ie}\,\cancelto{\mathbb{R}_{ee}\,\mathbb{H}_{ei}\,\mathbb{C}_i}{\mathbb{C}_e}$$

$$\Longrightarrow \left(\mathbb{H}_{ii} + \underbrace{\mathbb{H}_{ie}\,\mathbb{R}_{ee}\,\mathbb{H}_{ei}}_{\mathbb{V}_{ii}}\right)\mathbb{C}_i = E\,\mathbb{C}_i$$

E

$E =$

$$E = \mathbb{C}_i^{\dagger}\left(\mathbb{H}_{ii} + \mathbb{V}_{ii}\right)\mathbb{C}_i$$

$$E = \mathbb{C}_i^\dagger(\mathbb{H}_{ii} + \mathbb{V}_{ii})\mathbb{C}_i$$

$$= \langle \Psi_i | H | \Psi_i \rangle$$

$$E = \mathbb{C}_i^\dagger \left(\mathbb{H}_{ii} + \mathbb{V}_{ii} \right) \mathbb{C}_i$$

$$= \langle \Psi_i | H | \Psi_i \rangle + \langle \Psi_i | H | \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e | H | \Psi_i \rangle$$

$$E = \mathbb{c}_i^{\dagger}(\mathbb{H}_{ii} + \mathbb{V}_{ii})\mathbb{c}_i$$

$$= \langle \Psi_i | H | \Psi_i \rangle + \langle \Psi_i | H \underbrace{| \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e |}_{R_{ee}} H | \Psi_i \rangle$$

Example:

Example: CIS

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$\oint_i$

Example: CIS

$$\Phi_i = [\Phi\ \Phi_1]$$

Example: CIS

$$\Phi_i = [\Phi \ \Phi_1]$$

Ψ_i

Example: CIS

$$\Phi_i = [\Phi \; \Phi_1]$$

$$\Psi_i = c_1 \Phi$$

Example: CIS

$$\Phi_i = [\Phi \; \Phi_1]$$

$$\Psi_i = c_1 \Phi$$

$$E - E_{CIS}$$

Example: CIS

$$\Phi_i = [\Phi \ \Phi_1]$$

$$\Psi_i = c_1 \Phi$$

$$E - E_{CIS} =$$

Example: CIS

$$\Phi_i = \left[\Phi \ \ \Phi_1\right]$$

$$\Psi_i = C_1 \Phi$$

$$E - E_{CIS} = \langle \Phi | C_1^{\dagger} H | \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e | H C_1 | \Phi \rangle$$

Example: CIS

$$\Phi_i = [\Phi \ \Phi_1]$$

$$\Psi_i = C_1 \Phi$$

$$E - E_{CIS} = \langle \Phi | C_1^{\dagger} H | \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e | H C_1 | \Phi \rangle$$

$$\langle \Phi_e | H C_1 | \Phi \rangle$$

Example: CIS

$$\Phi_i = [\Phi \ \Phi_1]$$

$$\Psi_i = C_1 \Phi$$

$$E - E_{CIS} = \langle \Phi | C_1^{\dagger} H | \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e | H C_1 | \Phi \rangle$$

$$\langle \Phi_e | H C_1 | \Phi \rangle = \langle \Phi_2 \ \Phi_3 | V_c C_1 | \Phi \rangle$$

Example: CIS

$$\Phi_i = [\Phi \ \Phi_1]$$

$$\Psi_i = C_1 \Phi$$

$$E - E_{CIS} = \langle \Phi | C_1^\dagger H | \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e | H C_1 | \Phi \rangle$$

$$\langle \Phi_e | H C_1 | \Phi \rangle = \langle \Phi_2 \Phi_3 | V_c C_1 | \Phi \rangle$$

$E - H$

Example: CIS

$$\Phi_i = [\Phi\ \Phi_1]$$

$$\Psi_i = C_1 \Phi$$

$$E - E_{CIS} = \langle \Phi | C_1^\dagger H | \Phi_e \rangle \langle \Phi_e | E - H | \Phi_e \rangle^{-1} \langle \Phi_e | H C_1 | \Phi \rangle$$

$$\langle \Phi_e | H C_1 | \Phi \rangle = \langle \Phi_2\ \Phi_3 | V_c C_1 | \Phi \rangle$$

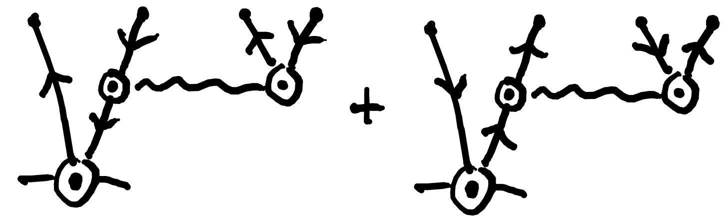
$$E - H \approx -H_0$$

$E - E_{cis}$

$$E - E_{CIS} \approx \left(\frac{1}{2!}\right)^2 \sum_{\substack{ab \\ ij}} \frac{|\langle \Phi_{ij}^{ab} | V_c C_1 | \Phi \rangle|^2}{\varepsilon_{ab}^{ij}}$$

$$E - E_{CIS} \approx \left(\frac{1}{2!}\right)^2 \sum_{\substack{ab \\ ij}} \frac{|\langle \Phi_{ij}^{ab} | V_c C_1 | \Phi \rangle|^2}{\varepsilon_{ab}^{ij}}$$

$$+ \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc \\ ijk}} \frac{|\langle \Phi_{ijk}^{abc} | V_c C_1 | \Phi \rangle|^2}{\varepsilon_{abc}^{ijk}}$$



$$E - E_{CIS} \approx \left(\frac{1}{2!}\right)^2 \sum_{\substack{ab\\ij}} \frac{|\langle \Phi_{ij}^{ab} | V_c C_1 | \Phi \rangle|^2}{\varepsilon_{ab}^{ij}}$$

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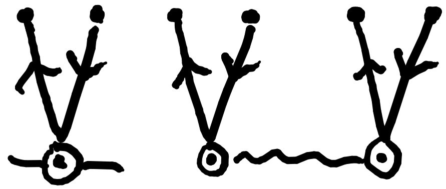

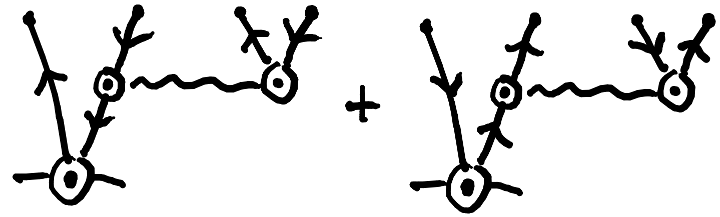

$$E - E_{CIS} \approx \left(\frac{1}{2!}\right)^2 \sum_{\substack{ab\\ij}} \frac{\left|\langle \Phi_{ij}^{ab} | V_c C_1 | \Phi \rangle\right|^2}{\varepsilon_{ab}^{ij}} + \left(\frac{1}{3!}\right)^2 \sum_{\substack{abc\\ijk}} \frac{\left|\langle \Phi_{ijk}^{abc} | V_c C_1 | \Phi \rangle\right|^2}{\varepsilon_{abc}^{ijk}}$$

the end.