A Faà di Bruno's formula

Theorem A.1. ***Faà di Bruno's formula.***

$$\frac{\partial^n}{\partial x_1 \cdots \partial x_n} f(g(\boldsymbol{x})) = \sum_{k=1}^{n} \sum_{(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_k)}^{\mathcal{P}_k(\boldsymbol{x})} f^{(k)}(g(\boldsymbol{x})) \prod_{i=1}^{k} \frac{\partial^{|\boldsymbol{x}_i|} g(\boldsymbol{x})}{\partial x_{i,1} \cdots \partial x_{i,|\boldsymbol{x}_i|}} \tag{A.1}$$

B Direct proof of the Hausdorff expansion

Proposition B.1. ***Nested commutator relation.*** $[X,\,\cdot\,]^n(Y) = \sum_{k=0}^{n} (-)^k \binom{n}{k} X^{n-k} Y X^k$.

Proof: We proceed by induction on n. For $n = 1$ this follows from the definition of the commutator, $[X, Y] = XY - YX$. Assuming the proposition holds for $n - 1$ nested commutators, we can express the n-fold nested commutator as

$$[X,\,\cdot\,]^n(Y) = X[X,\,\cdot\,]^{n-1}(Y) - [X,\,\cdot\,]^{n-1}(Y)\,X = X^k Y + \sum_{k=1}^{n-1} (-)^k \left(\binom{n-1}{k} + \binom{n-1}{k-1} \right) X^{n-k} Y X^k + (-)^n Y X^n$$

by expanding $[X,\,\cdot\,]^{n-1}(Y)$ twice and substituting k for $k - 1$ in the second summation. Combining factorials as follows

$$\binom{n-1}{k} + \binom{n-1}{k-1} = \frac{n-k}{n-k} \cdot \frac{(n-1)!}{k!(n-1-k)!} + \frac{k}{k} \cdot \frac{(n-1)!}{(k-1)!(n-k)!} = \binom{n}{k}$$

shows that the proposition also holds for n, completing the proof by induction.

Theorem B.1. ***The Hausdorff Expansion.*** $e^X Y e^{-X} = \sum_{n=0}^{\infty} \frac{1}{n!} [X,\,\cdot\,]^n(Y)$

Proof: This follows from a direct Taylor expansion of the exponentials, along with proposition B.1.[1]

$$e^X Y e^{-X} = \sum_{h=0}^{\infty} \sum_{k=0}^{\infty} \frac{1}{h!\,k!} (-)^k X^h Y X^k = \sum_{n=0}^{\infty} \frac{1}{n!} \sum_{k=0}^{n} \frac{n!}{(n-k)!\,k!} (-)^k X^{n-k} Y X^k = \sum_{n=0}^{\infty} \frac{1}{n!} [X,\,\cdot\,](Y)$$

In the second step, we have rearranged the sum to run over $n = h + k$ and k and inserted $1 = n!/n!$.

C Löwdin partitioning matrix derivation

Remark C.1. ***Löwdin partitioning.*** For a given truncation level m, let us refer to the span of $\boldsymbol{\Phi}_\mathrm{i} = \begin{bmatrix}\Phi \;\boldsymbol{\Phi}_1 \cdots \boldsymbol{\Phi}_m\end{bmatrix}$ as the *internal space* and that of $\boldsymbol{\Phi}_\mathrm{e} = \begin{bmatrix}\boldsymbol{\Phi}_{m+1} \cdots \boldsymbol{\Phi}_n\end{bmatrix}$ as the *external space*, so that $|\boldsymbol{\Phi}_\mathrm{i}\rangle\langle\boldsymbol{\Phi}_\mathrm{i}| + |\boldsymbol{\Phi}_\mathrm{e}\rangle\langle\boldsymbol{\Phi}_\mathrm{e}| = 1_n$. In the coordinate space over $\boldsymbol{\Phi}$ this reads $\mathbf{1}_\mathrm{i} + \mathbf{1}_\mathrm{e} = \mathbf{1}$, in terms of the following projection matrices.

$$\mathbf{1}_\mathrm{i} \equiv \langle\boldsymbol{\Phi}|\boldsymbol{\Phi}_\mathrm{i}\rangle\langle\boldsymbol{\Phi}_\mathrm{i}|\boldsymbol{\Phi}\rangle = \begin{bmatrix}\mathbf{1} & \mathbf{0}\\ \mathbf{0} & \mathbf{0}\end{bmatrix} \qquad \mathbf{1}_\mathrm{e} \equiv \langle\boldsymbol{\Phi}|\boldsymbol{\Phi}_\mathrm{e}\rangle\langle\boldsymbol{\Phi}_\mathrm{e}|\boldsymbol{\Phi}\rangle = \begin{bmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \mathbf{1}\end{bmatrix} \tag{C.1}$$

This allows us to write vector decompositions as $\mathbf{c} = \mathbf{c}_\mathrm{i} + \mathbf{c}_\mathrm{e}$ and matrix decompositions as $\mathbf{H} = \mathbf{H}_\mathrm{ii} + \mathbf{H}_\mathrm{ie} + \mathbf{H}_\mathrm{ei} + \mathbf{H}_\mathrm{ee}$ in terms of $\mathbf{c}_\mathrm{x} \equiv \mathbf{1}_\mathrm{x}\,\mathbf{c}$ and $\mathbf{H}_\mathrm{xy} \equiv \mathbf{1}_\mathrm{x}\,\mathbf{H}\,\mathbf{1}_\mathrm{y}$.[2] Finally, note that the *external space resolvent* $\mathbf{R}_\mathrm{ee} \equiv (E - \mathbf{H})^{-1}\big|_\mathrm{e}$ satisfies

$$\mathbf{R}_\mathrm{ee}\,(E - \mathbf{H}) = -\mathbf{R}_\mathrm{ee}\,\mathbf{H}_\mathrm{ei} + \mathbf{1}_\mathrm{e} \qquad (E - \mathbf{H})\,\mathbf{R}_\mathrm{ee} = -\mathbf{H}_\mathrm{ie}\,\mathbf{R}_\mathrm{ee} + \mathbf{1}_\mathrm{e} \tag{C.2}$$

and operating the left equation on $\mathbf{c}$ gives zero due to the Schrödinger equation, implying that $\mathbf{c}_\mathrm{e} = \mathbf{R}_\mathrm{ee}\mathbf{H}_\mathrm{ei}\mathbf{c}_\mathrm{i}$. Projecting the Schrödinger equation by $\mathbf{1}_\mathrm{i}$ and substituting in this expression for $\mathbf{c}_\mathrm{e}$ then leads to

$$(\mathbf{H}_\mathrm{ii} + \mathbf{V}_\mathrm{ii})\mathbf{c}_\mathrm{i} = E\mathbf{c}_\mathrm{i} \qquad \mathbf{V}_\mathrm{ii} \equiv \mathbf{H}_\mathrm{ie}\mathbf{R}_\mathrm{ee}\mathbf{H}_\mathrm{ei} \tag{C.3}$$

which reduces the Schrödinger equation on $\mathcal{F}_n$ to an effective Schrödinger equation in the internal space. This gives

$$E = \frac{\mathbf{c}_\mathrm{i}^\dagger(\mathbf{H}_\mathrm{ii} + \mathbf{V}_\mathrm{ii})\mathbf{c}_\mathrm{i}}{\mathbf{c}_\mathrm{i}^* \cdot \mathbf{c}_\mathrm{i}} \tag{C.4}$$

which expresses the exact energy in terms of internal-space coefficients. Let us refer to this energy expression as the *Löwdin functional*. The Löwdin functional is the central equation in the *Löwdin partitioning* method, which can be used to eliminate the leading error incurred by truncating at a given excitation level $m < n$.

[1] For a slick alternative to this proof, see Helgaker, Jørgensen, and Olsen, *Molecular Electronic-Structure Theory* (2000), p. 100.

[2] Note that I am dropping the subscript e on the Hamiltonian and energy here to avoid confusion with e.

D Löwdin partitioning for CI

Remark D.1. $\Psi_{\mathrm{i}}^{[\lceil m/2\rceil]} = \Psi_{\mathrm{CIS}\cdots m}$ and $(E - H_e)^{(0)} = -H_0$

$$E - E_{\mathrm{CIS}\cdots m} \approx \langle \Psi_{\mathrm{CIS}\cdots m} | V_{\mathrm{c}} | \mathbf{\Phi}_{\mathrm{e}} \rangle \langle \mathbf{\Phi}_{\mathrm{e}} | E_{\mathrm{c}} - H_{\mathrm{c}} | \mathbf{\Phi}_{\mathrm{e}} \rangle^{-1} \langle \mathbf{\Phi}_{\mathrm{e}} | V_{\mathrm{c}} | \Psi_{\mathrm{CIS}\cdots m} \rangle \tag{D.1}$$

$$E - E_{\mathrm{CIS}\cdots m} = (\tfrac{1}{(m+1)!})^2 \sum_{\substack{a_1\cdots a_{m+1} \\ i_1\cdots i_{m+1}}} \frac{|\langle \Phi_{i_1\cdots i_{m+1}}^{a_1\cdots a_{m+1}} | V_{\mathrm{c}}\,(C_{m-1} + C_m) | \Phi \rangle|^2}{\mathcal{E}_{a_1\cdots a_{m+1}}^{i_1\cdots i_{m+1}}} + (\tfrac{1}{(m+2)!})^2 \sum_{\substack{a_1\cdots a_{m+2} \\ i_1\cdots i_{m+2}}} \frac{|\langle \Phi_{i_1\cdots i_{m+2}}^{a_1\cdots a_{m+2}} | V_{\mathrm{c}}\, C_m | \Phi \rangle|^2}{\mathcal{E}_{a_1\cdots a_{m+2}}^{i_1\cdots i_{m+2}}} \tag{D.2}$$

E EOM-CC matrix equations

Remark E.1. Note that the EOM-CC equations can be expressed in matrix notation as

$$\overline{\mathbf{H}}_e \mathbf{r}_k = E_k \mathbf{r}_k \qquad \mathbf{l}_k^\dagger \overline{\mathbf{H}}_e = \mathbf{l}_k^\dagger E_k \qquad \mathbf{l}_k^* \cdot \mathbf{r}_l = \delta_{kl} \qquad \overline{\mathbf{H}}_e = \begin{bmatrix} E_e & \langle \Phi | \overline{H}_e | \mathbf{\Phi}_1 \rangle & \langle \Phi | \overline{H}_e | \mathbf{\Phi}_2 \rangle & \cdots \\ 0 & \langle \mathbf{\Phi}_1 | \overline{H}_e | \mathbf{\Phi}_1 \rangle & \langle \mathbf{\Phi}_1 | \overline{H}_e | \mathbf{\Phi}_2 \rangle & \cdots \\ 0 & \langle \mathbf{\Phi}_2 | \overline{H}_e | \mathbf{\Phi}_1 \rangle & \langle \mathbf{\Phi}_2 | \overline{H}_e | \mathbf{\Phi}_2 \rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \tag{E.1}$$

where we can identify the ground-state right eigenvector by inspection as $\mathbf{r}_0 = \langle \mathbf{\Phi} | \Phi \rangle$ with eigenvalue E_e.

F Frantz-Mills factorization theorem

Definition F.1. ***Level.*** Products of operators and resolvents are represented by graphs with resolvent lines. When each resolvent line spans the width of the diagram, we can partition a graph's operators into distinct *levels* numbered from bottom to top with zero indexing. An operator lies in the k^{th} level if there are k resolvent lines below it. A line originating in the k^{th} level and terminating in the k'^{th} level crosses the i^{th} resolvent line if $\min(k, k') < i \leq \max(k, k')$.

Definition F.2. ***Resolvent graph.*** A *resolvent graph* $R \equiv (G, m, \rho)$ partitions G's operators into m distinct levels, placing the operator o in level $\rho(o) \in \mathbb{Z}_m$ through the *level map*, ρ.[3]

Definition F.3. ***Substitution.*** Let $G[H \mapsto o\,]$ denote the *substitution* of a connected subgraph H in G with an operator o containing the same number of open cycles. An analogous operation, $R[S \mapsto o\,]$, can be performed for resolvent graphs. Let $R_k = (G_k, \rho_k, k+2)$ denote the substitution of everything above the k^{th} resolvent line in R by a single operator, $\widetilde{o}_{k+1}$.

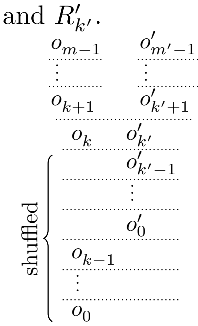
Remark F.1. A product of graphs $G = (L, O, h, t)$ and $G' = (L', O', h', t')$ forms a new graph given by

$$GG' = (L \cup L', O \cup O', h \oplus h', t \oplus t') \tag{F.1}$$

where $h \oplus h'$ acts as h on lines from L and as h' on lines from L'. The combined tail function is defined similarly.

Definition F.4. ***Zipper graph.*** A *zipper graph* $(RR')_\pi^{k,k'}$ joins R and R' at levels k and k' and interleaves their lower levels with a riffle-shuffle $\pi \in \mathrm{S}_{\mathbb{Z}_{k+k'}}^{(k,k')}$. Formally, the zipper graph is defined as follows, in terms of R_k and $R'_{k'}$.

$$(RR')_\pi^{k,k'} \equiv (G_k G'_{k'},\ k + k' + 2,\ \rho_\pi^{k,k'}) \qquad \begin{aligned} \rho_\pi^{k,k'}(o') &= \begin{cases} \rho'_{k'}(o') + k & \rho'_{k'}(o') \geq k' \\ \pi(\rho'_{k'}(o') + k) & \rho'_{k'}(o') < k' \end{cases} \qquad o' \in O' \\ \rho_\pi^{k,k'}(o\,) &= \begin{cases} \rho_k(o) + k' & \rho_k(o) \geq k \\ \pi(\rho_k(o)) & \rho_k(o) < k \end{cases} \qquad o \in O \end{aligned}$$



The diagram on the right displays the structure of a zipper graph, assuming that R and R' have one operator per level. The two subgraphs above the combined level correspond to $\widetilde{o}_{k+1}$ and $\widetilde{o}'_{k'+1}$ in R_k and $R'_{k'}$.

Theorem F.1. ***The Frantz-Mills factorization theorem.*** $RR' = \sum_\pi (RR')_\pi^{k,k'}$

Proof:

Definition F.5. ***Insertion graph.***

[3] $\mathbb{Z}_m$ denotes the first m nonnegative integers, $\{0, 1, \ldots, m-1\}$. Note that an m-level resolvent graph contains $m-1$ resolvents.