

A Faà di Bruno's formula

Theorem A.1. Faà di Bruno's formula.

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

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

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

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 $\Phi_i = [\Phi \Phi_1 \cdots \Phi_m]$ as the *internal space* and that of $\Phi_e = [\Phi_{m+1} \cdots \Phi_n]$ as the *external space*, so that $|\Phi_i\rangle\langle\Phi_i| + |\Phi_e\rangle\langle\Phi_e| = 1_n$. In the coordinate space over Φ this reads $\mathbf{1}_i + \mathbf{1}_e = \mathbf{1}$, in terms of the following projection matrices.

$$\mathbf{1}_i \equiv \langle\Phi|\Phi_i\rangle\langle\Phi_i|\Phi\rangle = \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{bmatrix} \quad \mathbf{1}_e \equiv \langle\Phi|\Phi_e\rangle\langle\Phi_e|\Phi\rangle = \begin{bmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{bmatrix} \quad (\text{C.1})$$

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

$$\mathbf{R}_{ee} (E - \mathbf{H}) = -\mathbf{R}_{ee} \mathbf{H}_{ei} + \mathbf{1}_e \quad (E - \mathbf{H}) \mathbf{R}_{ee} = -\mathbf{H}_{ie} \mathbf{R}_{ee} + \mathbf{1}_e \quad (\text{C.2})$$

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

$$(\mathbf{H}_{ii} + \mathbf{V}_{ii}) \mathbf{c}_i = E \mathbf{c}_i \quad \mathbf{V}_{ii} \equiv \mathbf{H}_{ie} \mathbf{R}_{ee} \mathbf{H}_{ei} \quad (\text{C.3})$$

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

$$E = \frac{\mathbf{c}_i^\dagger (\mathbf{H}_{ii} + \mathbf{V}_{ii}) \mathbf{c}_i}{\mathbf{c}_i^* \cdot \mathbf{c}_i} \quad (\text{C.4})$$

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 $m < n$.

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

²Note 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. $\Psi_1^{[\lceil m/2 \rceil]} = \Psi_{\text{CIS}\dots m}$ and $(E - H)^{(0)} = -H_0$

$$E - E_{\text{CIS}\dots m} \approx \langle \Psi_{\text{CIS}\dots m} | V_c | \Phi_e \rangle \langle \Phi_e | E_c - H_c | \Phi_e \rangle^{-1} \langle \Phi_e | V_c | \Psi_{\text{CIS}\dots m} \rangle \quad (\text{D.1})$$

$$E - E_{\text{CIS}\dots m} = \left(\frac{1}{(m+1)!}\right)^2 \sum_{\substack{a_1 \dots a_{m+1} \\ i_1 \dots i_{m+1}}} \frac{|\langle \Phi_{i_1 \dots i_{m+1}}^{a_1 \dots a_{m+1}} | V_c (C_{m-1} + C_m) | \Phi \rangle|^2}{\mathcal{E}_{a_1 \dots a_{m+1}}^{i_1 \dots i_{m+1}}} + \left(\frac{1}{(m+2)!}\right)^2 \sum_{\substack{a_1 \dots a_{m+2} \\ i_1 \dots i_{m+2}}} \frac{|\langle \Phi_{i_1 \dots i_{m+2}}^{a_1 \dots a_{m+2}} | V_c C_m | \Phi \rangle|^2}{\mathcal{E}_{a_1 \dots a_{m+2}}^{i_1 \dots i_{m+2}}} \quad (\text{D.2})$$

E EOM-CC matrix equations

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

$$\begin{aligned} \bar{\mathbf{H}} \mathbf{r}_k &= E_k \mathbf{r}_k & \mathbf{l}_k^\dagger \bar{\mathbf{H}} &= \mathbf{l}_k^\dagger E_k & \mathbf{l}_k^* \cdot \mathbf{r}_l &= \delta_{kl} & \bar{\mathbf{H}} &= \begin{bmatrix} E & \langle \Phi | \bar{H} | \Phi_1 \rangle & \langle \Phi | \bar{H} | \Phi_2 \rangle & \dots \\ 0 & \langle \Phi_1 | \bar{H} | \Phi_1 \rangle & \langle \Phi_1 | \bar{H} | \Phi_2 \rangle & \dots \\ 0 & \langle \Phi_2 | \bar{H} | \Phi_1 \rangle & \langle \Phi_2 | \bar{H} | \Phi_2 \rangle & \dots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix} \end{aligned} \quad (\text{E.1})$$

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

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

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 $\pi \in S_{\mathbb{Z}_{k+k'}}^{(k, k')}$. Formally, the zipper graph is defined as follows, in terms of R_k and $R'_{k'}$.

$$(RR')_{\pi}^{k, k'} \equiv (G_k G'_{k'}, k + k' + 2, \rho_{\pi}^{k, k'})$$

$$\rho_{\pi}^{k, k'}(o') = \begin{cases} \rho'_{k'}(o') + k & \rho'_{k'}(o') \geq k' \\ \pi(\rho'_{k'}(o') + k) & \rho'_{k'}(o') < k' \end{cases} \quad o' \in O'$$

$$\rho_{\pi}^{k, k'}(o) = \begin{cases} \rho_k(o) + k' & \rho_k(o) \geq k \\ \pi(\rho_k(o)) & \rho_k(o) < k \end{cases} \quad o \in O$$

shuffled

o_{m-1}
 $o'_{m'-1}$

\vdots
 \vdots

o_{k+1}
 $o'_{k'+1}$

o_k
 $o'_{k'}$

\vdots
 \vdots

$o_{k'-1}$
 $o'_{k'-1}$

\vdots
 \vdots

o_0
 o'_0

\vdots
 \vdots

o_{k-1}
 o'_{k-1}

\vdots
 \vdots

o_0
 o'_0

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 \tilde{o}_{k+1} and $\tilde{o}'_{k'+1}$ 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, $\{0, 1, \dots, m-1\}$. Note that an m -level resolvent graph contains $m-1$ resolvents.

G Orbital optimization

$$H = h_p^q a_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} a_{rs}^{pq} \quad (\text{G.1})$$

$$E = h_p^q \gamma_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \gamma_{rs}^{pq} \quad (\text{G.2})$$

$$\mathcal{L} = \text{Re}(h_p^q \bar{\gamma}_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \bar{\gamma}_{rs}^{pq}) \quad \begin{aligned} \bar{\gamma}_q^p &\equiv \langle \Phi | (1 + \Lambda) a_q^p \exp(T) | \Phi \rangle_C \\ \bar{\gamma}_{rs}^{pq} &\equiv \langle \Phi | (1 + \Lambda) a_{rs}^{pq} \exp(T) | \Phi \rangle_C \end{aligned} \quad (\text{G.3})$$

$$\mathcal{L} = h_p^q \gamma_q^p + \frac{1}{4} \bar{g}_{pq}^{rs} \gamma_{rs}^{pq} \quad \begin{aligned} \gamma_q^p &\equiv \frac{1}{2} (\bar{\gamma}_q^p + \bar{\gamma}_p^{q*}) \\ \gamma_{rs}^{pq} &\equiv \frac{1}{2} (\bar{\gamma}_{rs}^{pq} + \bar{\gamma}_{pq}^{rs*}) \end{aligned} \quad (\text{G.4})$$

H ROHF

Let ϕ_d , ϕ_s , and ϕ_v be column vectors of doubly occupied, singly occupied, and virtual orbitals. Each of these spatial functions corresponds to two spin-orbital vectors, $\phi_x \alpha$ and $\phi_x \beta$, and the SODS-ROHF effective Fock operator is given (in the Guest-Saunders approach) by the following

$$\hat{f}_{\text{eff}} \equiv \begin{pmatrix} \hat{1}_d & \hat{1}_s & \hat{1}_v \end{pmatrix} \begin{pmatrix} \hat{f}_{\text{avg}} & \hat{f}_\beta & \hat{f}_{\text{avg}} \\ \hat{f}_\beta & \hat{f}_{\text{avg}} & \hat{f}_\alpha \\ \hat{f}_{\text{avg}} & \hat{f}_\alpha & \hat{f}_{\text{avg}} \end{pmatrix} \begin{pmatrix} \hat{1}_d \\ \hat{1}_s \\ \hat{1}_v \end{pmatrix} \quad \hat{f}_{\text{avg}} \equiv \frac{1}{2} (\hat{f}_\alpha + \hat{f}_\beta) \quad \hat{1}_x \equiv |\psi_x\rangle \langle \psi_x| \quad (\text{H.1})$$

where \hat{f}_α and \hat{f}_β are the usual Fock operators, defined in terms of \hat{f}_{eff} 's self-consistent densities.

Start with the canonical Hartree-Fock equation

$$\hat{f}_{\text{eff}} \phi_p = \epsilon_p \phi_p \quad \hat{f}_{\text{eff}} = \sum_{x,y} \hat{1}_x \hat{f}_{\text{eff}}^{x,y} \hat{1}_y \quad (\text{H.2})$$

and expand it in the AO basis.

$$\langle \chi | \hat{f}_{\text{eff}} | \chi \rangle \mathbf{c}_p = \epsilon_p \langle \chi | \chi \rangle \mathbf{c}_p \quad \hat{1}_x = |\phi_x\rangle \langle \phi_x| = |\chi\rangle \mathbf{C}_x \mathbf{C}_x^\dagger \langle \chi| \quad (\text{H.3})$$

Yields the following

$$\langle \chi | \hat{f}_{\text{eff}} | \chi \rangle = \sum_{x,y} \mathbf{P}_x^\dagger \langle \chi | \hat{f}_{\text{eff}}^{x,y} | \chi \rangle \mathbf{P}_y \quad \mathbf{P}_x \equiv \mathbf{C}_x \mathbf{C}_x^\dagger \langle \chi | \chi \rangle \quad (\text{H.4})$$

designating the single occupations as alpha spins, we have the following relationships

$$\mathbf{P}_d = \mathbf{D}_\beta \mathbf{S} \quad \mathbf{P}_{s+d} = \mathbf{D}_\alpha \mathbf{S} \quad \hat{1}_s = \hat{1} - \hat{1}_d \quad \hat{1}_v = \hat{1} - \hat{1}_{s+d} \quad (\text{H.5})$$

where $\mathbf{D}_\beta = \mathbf{C}_{o_\beta} \mathbf{C}_{o_\beta}^\dagger$ and $\mathbf{D}_\alpha = \mathbf{C}_{o_\alpha} \mathbf{C}_{o_\alpha}^\dagger$ are the UHF density matrices. This allows us to express the AO-basis pseudo-projection operators as follows.

$$\mathbf{P}_d = \mathbf{D}_\beta \mathbf{S} \quad \mathbf{P}_s = (\mathbf{D}_\alpha - \mathbf{D}_\beta) \mathbf{S} \quad \mathbf{P}_v = \mathbf{1} - \mathbf{D}_\alpha \mathbf{S} \quad (\text{H.6})$$

The final expression for the effective Fock matrix in terms of UHF Fock matrices is as follows.

$$\mathbf{F}_{\text{eff}} = \frac{1}{2} \sum_{\substack{x,y \in \{d,v\} \\ x=y=s}} \mathbf{P}_x^\dagger (\mathbf{F}_\alpha + \mathbf{F}_\beta) \mathbf{P}_y + \sum_{x \neq y \in \{d,s\}} \mathbf{P}_x \mathbf{F}_\beta \mathbf{P}_y + \sum_{x \neq y \in \{s,v\}} \mathbf{P}_x \mathbf{F}_\alpha \mathbf{P}_y \quad (\text{H.7})$$