ForteCon 2019 – Notes on DSRG-MRPT2

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1 Orbital Notation

We first introduce the orbital notations used in this note, shown in Fig. 1.1. For single-reference cases, the set of molecular spin orbitals (MO, **G**) is partitioned into four parts: frozen core (**FC**) with labels I, J, K, L, M, N, occupied (**O**) with labels i, j, k, l, m, n, virtual (**V**) with labels a, b, c, d, e, f, and frozen virtual (**FV**) with labels A, B, C, D, E, F. For multireference cases, we generally have five orbital spaces where the correlated orbitals are separated into core (**C**), active (**A**), and virtual (**V**) spaces. We also introduce the composite orbital spaces: hole ($\mathbf{H} = \mathbf{C} \cup \mathbf{A}$) and particle ($\mathbf{P} = \mathbf{A} \cup \mathbf{V}$). We use indices i, j, k, l for **H**; a, b, c, d for **P**; m, n for **C**; e, f for **V**; and u, v, w, x, y, z for **A**.

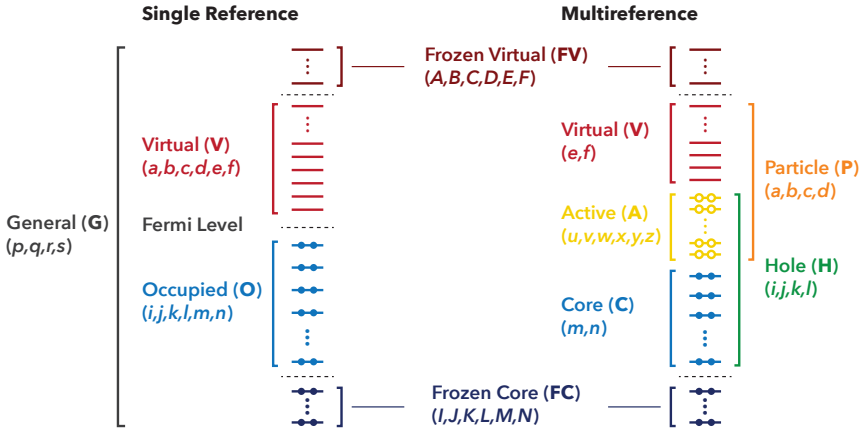

Figure 1.1: Partitioning of the spin orbital basis and corresponding orbital indices adopted in this note.

In cases where we integrate over spin coordinates, we will augment the indices with a subscript $\uparrow$ (or $\downarrow$) to denote α (or β) spin. For spin-adapted indices, I will add a bar on top of the index, for example, $\bar{p}$.

2 MP2 energy expression

The MP2 correlation energy (in canonical orbital basis) is given by

$$E_{\mathrm{MP2}} = \frac{1}{4} \sum_{ij} \sum_{ab} \langle ij \| ab \rangle \, t_{ab}^{ij} \equiv \frac{1}{4} v_{ij}^{ab} t_{ab}^{ij}, \tag{2.1}$$

where $v_{ij}^{ab} \equiv \langle ij \| ab \rangle = \langle ij | ab \rangle - \langle ij | ba \rangle$ are the antisymmetrized two-electron integrals in physicists' notation. The MP2 amplitudes t_{ab}^{ij} are given by

$$t_{ab}^{ij} = \frac{\langle ij \| ab \rangle}{\Delta_{ab}^{ij}}, \quad \Delta_{ab}^{ij} \equiv \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b, \tag{2.2}$$

where the denominators Δ_{ab}^{ij} are expressed in terms of orbital energies ε_p. We adopt the Einstein summation convention over repeated indices in Eq. (3.1) and wherever possible in the following text.

Note: *You can try to implement the spin-orbital version of MP2 by yourself. In this case, you need to use spin-integrated integrals from Forte to build your own spin-orbitals integrals. To debug your code, it is a good practice to find several equivalent representations and match the results.*

We now integrate over spins by rewriting the MP2 energy expression as

$$\begin{aligned} E_{\mathrm{MP2}} &= \frac{1}{4} v_{i_\uparrow j_\uparrow}^{a_\uparrow b_\uparrow} t_{a_\uparrow b_\uparrow}^{i_\uparrow j_\uparrow} + \frac{1}{4} v_{i_\downarrow j_\downarrow}^{a_\downarrow b_\downarrow} t_{a_\downarrow b_\downarrow}^{i_\downarrow j_\downarrow} + \frac{1}{4} v_{i_\uparrow j_\downarrow}^{a_\uparrow b_\downarrow} t_{a_\uparrow b_\downarrow}^{i_\uparrow j_\downarrow} + \frac{1}{4} v_{i_\uparrow j_\downarrow}^{a_\downarrow b_\uparrow} t_{a_\downarrow b_\uparrow}^{i_\uparrow j_\downarrow} + \frac{1}{4} v_{i_\downarrow j_\uparrow}^{a_\downarrow b_\uparrow} t_{a_\downarrow b_\uparrow}^{i_\downarrow j_\uparrow} + \frac{1}{4} v_{i_\downarrow j_\uparrow}^{a_\uparrow b_\downarrow} t_{a_\uparrow b_\downarrow}^{i_\downarrow j_\uparrow} \\ &= \frac{1}{4} v_{i_\uparrow j_\uparrow}^{a_\uparrow b_\uparrow} t_{a_\uparrow b_\uparrow}^{i_\uparrow j_\uparrow} + \frac{1}{4} v_{i_\downarrow j_\downarrow}^{a_\downarrow b_\downarrow} t_{a_\downarrow b_\downarrow}^{i_\downarrow j_\downarrow} + v_{i_\uparrow j_\downarrow}^{a_\uparrow b_\downarrow} t_{a_\uparrow b_\downarrow}^{i_\uparrow j_\downarrow}, \end{aligned} \tag{2.3}$$

where the second line is obtained by relabeling indices and using the antisymmetry in v_{ij}^{ab} and t_{ab}^{ij} ($v_{ij}^{ab} = -v_{ij}^{ba} = -v_{ji}^{ab} = v_{ji}^{ba}$). In general, we need to *at least* derive the spin-integrated equations to have a fairly viable implementation of the method. Let us implement this version of MP2 using Forte for Numpy.

For a closed-shell reference, the MP2 energy equation can be further simplified since $p_\uparrow = p_\downarrow = \bar{p}$

$$v_{i_\uparrow j_\uparrow}^{a_\uparrow b_\uparrow} = v_{i_\downarrow j_\downarrow}^{a_\downarrow b_\downarrow} = \langle \bar{i}\bar{j} | \bar{a}\bar{b} \rangle - \langle \bar{i}\bar{j} | \bar{b}\bar{a} \rangle , \tag{2.4}$$

$$v_{i_\uparrow j_\downarrow}^{a_\uparrow b_\downarrow} = \langle \bar{i}\bar{j} | \bar{a}\bar{b} \rangle . \tag{2.5}$$

The MP2 energy expression then becomes

$$E_{\mathrm{MP2}} = \sum_{ij} \sum_{ab} \frac{\langle \bar{i}\bar{j} | \bar{a}\bar{b} \rangle \left(2 \langle \bar{i}\bar{j} | \bar{a}\bar{b} \rangle - \langle \bar{i}\bar{j} | \bar{b}\bar{a} \rangle \right)}{\Delta_{\bar{a}\bar{b}}^{\bar{i}\bar{j}}}. \tag{2.6}$$

This equation should look familiar to you as it is the one used in Crawford's programming exercises.

To conclude this section, note that these MP2 expressions are based on the Hartree–Fock reference and the canonical orbitals. For Hartree–Fock reference but non-canonical orbitals, the energy expression Eq. (3.1) remains the same but the amplitudes are determined by

$$0 = v_{ab}^{ij} + \mathcal{P}_-(a,b) f_a^c t_{cb}^{ij} - \mathcal{P}_-(i,j) f_k^i t_{ab}^{kj}, \tag{2.7}$$

where $\mathcal{P}_-(p,q) g(p,q) = g(p,q) - g(q,p)$ generates a term with swapped indices. You can entertain yourself by implementing this orbital-invariant MP2 using localized orbitals with the Fock matrix given by

$$f_p^q = h_p^q + \sum_i v_{pi}^{qi}. \tag{2.8}$$

For non-Hartree–Fock reference, singles amplitudes will appear as we will see for multireference cases.

3 DSRG-PT2 energy expression

The DSRG-PT2 energy expression is given by

$$E_{\text{DSRG-PT2}} = \frac{1}{4} \sum_{ij} \sum_{ab} v_{ab}^{ij} t_{ab}^{ij} \left(1 + e^{-s(\Delta_{ab}^{ij})^2} \right), \tag{3.1}$$

$$t_{ab}^{ij} = \frac{v_{ab}^{ij}}{\Delta_{ab}^{ij}} \left(1 - e^{-s(\Delta_{ab}^{ij})^2} \right). \tag{3.2}$$

Let us modify our MP2 code to get the DSRG-PT2 energy. Note that you may need to implement the Taylor expansion of the exponential in the amplitudes expression when Δ_{ab}^{ij} is close to zero.

One thing that I want to mention is point group symmetry. In Psi4, the orbitals are in Pitzer ordering, that is, orbitals are ordered according to irrep first and then orbital energies within each irrep. Let us now implement DSRG-PT2 with point group symmetry.

4 uDSRG-MRPT2 energy expression

The unrelaxed DSRG-MRPT2 equations look very similar to those of DSRG-PT2 but more tedious. To start with, we build the generalized Fock matrix (also called averaged Fock matrix)

$$f_p^q = h_p^q + v_{pi}^{qj}\gamma_j^i = h_p^q + \sum_m v_{pm}^{qm} + v_{pu}^{qv}\gamma_v^u. \tag{4.1}$$

In semicanonical basis, the diagonal blocks of the generalized Fock matrix are diagonal:

$$f_m^n = \varepsilon_m \delta_n^m, \quad f_u^v = \varepsilon_u \delta_v^u, \quad f_e^f = \varepsilon_e \delta_f^e. \tag{4.2}$$

The singles and doubles amplitudes are given by

$$t_a^i = \left[f_a^i + \sum_{ux} (\varepsilon_x - \varepsilon_u) t_{ax}^{iu} \gamma_u^x \right] \frac{1 - e^{-s\left(\Delta_a^i\right)^2}}{\Delta_a^i}, \tag{4.3}$$

$$t_{ab}^{ij} = v_{ab}^{ij} \frac{1 - e^{-s\left(\Delta_{ab}^{ij}\right)^2}}{\Delta_{ab}^{ij}}. \tag{4.4}$$

We also need to renormalize the one- and two-electron integrals

$$\tilde{f}_a^i = f_a^i \left[1 + e^{-s(\Delta_a^i)^2}\right] + e^{-s(\Delta_a^i)^2} \sum_{ux} \Delta_u^x t_{ax}^{iu}(s) \gamma_u^x, \tag{4.5}$$

$$\tilde{v}_{ab}^{ij} = v_{ab}^{ij} \left[1 + e^{-s(\Delta_{ab}^{ij})^2}\right]. \tag{4.6}$$

The uDSRG-MRPT2 energy expressions contain 11 terms:

$$\begin{aligned} E_{\text{uDSRG-MRPT2}} = {} & \tilde{f}_j^b t_a^i \gamma_i^j \eta_b^a + \frac{1}{2} \tilde{f}_x^e t_{ey}^{uv} \lambda_{uv}^{xy} - \frac{1}{2} \tilde{f}_m^v t_{xy}^{um} \lambda_{uv}^{xy} + \frac{1}{2} \tilde{v}_{xy}^{ev} t_e^u \lambda_{uv}^{xy} - \frac{1}{2} \tilde{v}_{my}^{uv} t_x^m \lambda_{uv}^{xy} + \frac{1}{4} \tilde{v}_{kl}^{cd} t_{ab}^{ij} \gamma_i^k \gamma_j^l \eta_c^a \eta_d^b \\ & + \frac{1}{8} \left(\tilde{v}_{xy}^{cd} t_{ab}^{uv} \eta_c^a \eta_d^b + \tilde{v}_{kl}^{uv} t_{xy}^{ij} \gamma_i^k \gamma_j^l \right) \lambda_{uv}^{xy} + \tilde{v}_{jx}^{vb} t_{ay}^{iu} \gamma_i^j \eta_b^a \lambda_{uv}^{xy} + \frac{1}{4} \left(\tilde{v}_{nz}^{uv} t_{xy}^{nw} + \tilde{v}_{xy}^{we} t_{ez}^{uv} \right) \lambda_{uvw}^{xyz}, \end{aligned} \tag{4.7}$$

where the one-particle (γ) and one-hole (η) satisfy the condition $\gamma_q^p + \eta_q^p = \delta_q^p$. The density cumulants are labeled as λ, which are provided by Forte, as well as γ. Note that one-particle density has a special structure for active-space based methods such that the core-core block is an identity matrix; the active-active block is a dense matrix; and every other blocks are zero:

$$\gamma_q^p = \begin{cases} \delta_q^p, & p, q \in \mathbf{C} \\ \lambda_q^p, & p, q \in \mathbf{A} \\ \text{otherwise} \end{cases} \tag{4.8}$$

The antisymmetry of $\tilde{v}_{pq}^{rs}$ and t_{ab}^{ij} and the fact that DSRG-MRPT2 does not contain internal excitations ($t_{uv}^{xy} = 0$) can also be used to simplify equations. For example, there are generally $2^4 - 1 = 15$ blocks in doubles amplitudes but many of them are redundant such as $t_{eu}^{mv} = t_{ue}^{vm} = -t_{ue}^{mv} = -t_{eu}^{vm}$. Therefore, there are only 8 blocks of doubles: $t_{ef}^{mn}, t_{eu}^{mn}, t_{ef}^{mu}, t_{uv}^{mn}, t_{ef}^{uv}, t_{eu}^{mv}, t_{eu}^{xy}$, and t_{xy}^{mu}. The amplitudes equations also suggests that to build these amplitudes, we only need the corresponding two-electron integrals. We can then form a dictionary to label these integrals and amplitudes.

I am not sure we can finish implementing all uDSRG-MRPT2 terms today, but I am hoping that we can finish term VI (which is MP2-like term). Anyway, I am giving all simplified equations below. Terms II–V, X and XI are in their simplified forms. Only term VI is automatically generated while others are derived by hand. Please let me know if you find any errors.

$$\text{I} = \tilde{f}_j^a t_a^i \gamma_i^j - \tilde{f}_j^v t_u^i \gamma_i^j \gamma_v^u = \tilde{f}_m^a t_a^m + \tilde{f}_v^a t_a^u \gamma_u^v - \tilde{f}_m^v t_u^m \gamma_v^u, \tag{4.9}$$

$$
\begin{aligned}
\mathrm{VI} = & \frac{1}{4}\tilde{v}^{ef}_{mn}t^{mn}_{ef} + \frac{1}{2}\tilde{v}^{eu}_{mn}t^{mn}_{eu} + \frac{1}{4}\tilde{v}^{mn}_{uv}t^{uv}_{mn} \\
& - \frac{1}{2}\tilde{v}^{eu}_{mn}t^{mn}_{ev}\gamma^{v}_{u} + \frac{1}{2}\tilde{v}^{ef}_{mu}t^{mv}_{ef}\gamma^{v}_{u} + \tilde{v}^{eu}_{mv}t^{mw}_{eu}\gamma^{w}_{v} - \frac{1}{2}\tilde{v}^{mn}_{uv}t^{uw}_{mn}\gamma^{w}_{v} + \frac{1}{2}\tilde{v}^{mu}_{vw}t^{vw}_{mx}\gamma^{x}_{u} \\
& - \tilde{v}^{eu}_{mv}t^{mx}_{ew}\gamma^{w}_{u}\gamma^{x}_{v} + \frac{1}{4}\tilde{v}^{ef}_{uv}t^{wx}_{ef}\gamma^{w}_{u}\gamma^{x}_{v} + \frac{1}{4}\tilde{v}^{mn}_{uv}t^{wx}_{mn}\gamma^{w}_{u}\gamma^{x}_{v} + \frac{1}{2}\tilde{v}^{eu}_{vw}t^{xy}_{eu}\gamma^{x}_{v}\gamma^{y}_{w} - \tilde{v}^{mu}_{vw}t^{vy}_{mx}\gamma^{x}_{u}\gamma^{y}_{w} \\
& - \frac{1}{2}\tilde{v}^{eu}_{vw}t^{yz}_{ex}\gamma^{x}_{u}\gamma^{y}_{v}\gamma^{z}_{w} + \frac{1}{2}\tilde{v}^{mu}_{vw}t^{yz}_{mx}\gamma^{x}_{u}\gamma^{y}_{v}\gamma^{z}_{w},
\end{aligned} \tag{4.10}
$$

$$
\mathrm{VII} = \frac{1}{8}\lambda^{xy}_{uv}\left(\tilde{v}^{ef}_{xy}t^{uv}_{ef} + 2\tilde{v}^{ew}_{xy}t^{uv}_{ew} - 2\tilde{v}^{ez}_{xy}t^{uv}_{ew}\gamma^{w}_{z}\right), \tag{4.11}
$$

$$
\mathrm{VIII} = \frac{1}{8}\lambda^{xy}_{uv}\left(\tilde{v}^{uv}_{mn}t^{mn}_{xy} + 2\tilde{v}^{uv}_{mz}t^{mw}_{xy}\gamma^{z}_{w}\right), \tag{4.12}
$$

$$
\mathrm{IX} = \left(\tilde{v}^{ve}_{mx}t^{mu}_{ey} + \tilde{v}^{vw}_{mx}t^{mu}_{wy} + \tilde{v}^{ve}_{zx}t^{wu}_{ey}\gamma^{z}_{w} - \tilde{v}^{vz}_{mx}t^{mu}_{wy}\gamma^{w}_{z}\right)\lambda^{xy}_{uv}. \tag{4.13}
$$

For terms VI, VII–IX, we can build common intermediates to reduce times for contraction. For example, $\tilde{v}^{ef}_{xy}t^{uv}_{ef}$ is found in both terms VI and VII. How to efficiently build these intermediates is still an open question for DSRG-MRPT2. When you finished, try to run benzyne with CAS(8,8) and the cc-pVTZ basis set and report your timings on the cluster!