Electronic Supplementary Information: Distinguishing Artificial and Essential Symmetry Breaking in a Single Determinant: Approach and Application to the C_{60}, C_{36}, and C_{20} Fullerenes

Joonho Lee* and Martin Head-Gordon*

Department of Chemistry, University of California, Berkeley, California 94720, USA

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

E-mail: linusjoonho@gmail.com; mhg@cchem.berkeley.edu

One-Particle Density Matrix of MP2

For OOMP2 methods, we compute the correlated 1PDM using

$$P_{ij}^{(2)} = -\frac{1}{2}\sum_{abk}(t_{ik}^{ab})^* t_{jk}^{ab} \tag{S1}$$

$$P_{ab}^{(2)} = \frac{1}{2}\sum_{ijc}(t_{ij}^{ac})^* t_{ij}^{bc}. \tag{S2}$$

where the first is the MP2 correction to the occupied-occupied (OO) block of the 1PDM and the second is the correction to the virtual-virtual (VV) block. For κ-OOMP2, the amplitudes used in Eq. (S1) and Eq. (S2) are regularized. Moreover, κ-OOMP2 has an extra term to the OO and VV blocks,

$$X_{ij} = -\kappa \int_0^1 \mathrm{d}\tau e^{\tau\kappa\epsilon_i}(\omega_{ij}^* + \omega_{ji})e^{(1-\tau)\kappa\epsilon_j} \tag{S3}$$

$$Y_{ab} = \kappa \int_0^1 \mathrm{d}\tau e^{-\tau\kappa\epsilon_a}(\omega_{ab} + \omega_{ba}^*)e^{-(1-\tau)\kappa\epsilon_b} \tag{S4}$$

where the definition of ω_{ij} and ω_{ab} are defined as follows:

$$\omega_{ij} = \sum_{aP} e^{-\tau\kappa\epsilon_a} V_{ia}^P \tilde{\Gamma}_{aj}^P \tag{S5}$$

and

$$\omega_{ab} = \sum_{iP} e^{\tau\kappa\epsilon_i} \tilde{\Gamma}_{ai}^P V_{ib}^P \tag{S6}$$

where V_{ia}^P is the 3-center 2-electron integrals and $\tilde{\Gamma}_{ai}^P$ reads

$$\tilde{\Gamma}_{ai}^P = \sum_{jb} t_{ij}^{ab} V_{jb}^P \tag{S7}$$

The resulting κ-OOMP2 1PDM is then obtained by summing the usual MP2 contribution and the regularization correction terms (Eq. (S3) and Eq. (S4)). In other words, we have

$$\tilde{P}_{ij}^{(2)} = P_{ij}^{(2)} + X_{ij} \tag{S8}$$

$$\tilde{P}_{ab}^{(2)} = P_{ab}^{(2)} + Y_{ab} \tag{S9}$$

These $\tilde{P}_{ij}^{(2)}$ and $\tilde{P}_{ab}^{(2)}$ are the *relaxed* 1PDMs of κ-OOMP2. More details are available in ref. 35.

Non-Collinearity Test of MP1 Wavefunctions

In order to perform the non-collinearity test on an MP1 wavefunction, one needs first-order corrections to $\langle \hat{S}_i \rangle$ and $\langle \hat{S}_i \hat{S}_j \rangle$ where $i, j \in \{x, y, z\}$. The first-order correction to $\langle \hat{O} \rangle$ for an operator $\hat{O}$ is defined as follows:

$$\langle\hat{O}\rangle_1 = \langle\Psi_1|\hat{O}|\Psi_0\rangle + \langle\Psi_0|\hat{O}|\Psi_1\rangle. \tag{S10}$$

This can be derived from the derivative with respect to λ of the first-order MP energy expression $E^{(1)}$ with a modified Hamiltonian, $\hat{H} + \lambda\hat{O}$. We enumerate the expectation value of each spin operator using this formula. For $\langle\hat{S}^2\rangle$, one may use the following identity:

$$\hat{S}^2 = \hat{S}_z + \hat{S}_z^2 + \hat{S}_-\hat{S}_+, \tag{S11}$$

where

$$\hat{S}_z = \frac{1}{2}\sum_p \left(\hat{a}^\dagger_{p_\alpha}\hat{a}_{p_\alpha} - \hat{a}^\dagger_{p_\beta}\hat{a}_{p_\beta}\right) \tag{S12}$$

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y = \sum_p \hat{a}^\dagger_{p_\alpha}\hat{a}_{p_\beta} \tag{S13}$$

$$\hat{S}_- = \hat{S}_x - i\hat{S}_y = \sum_p \hat{a}^\dagger_{p_\beta}\hat{a}_{p_\alpha} \tag{S14}$$

One can evaluate $\langle\hat{S}_i\hat{S}_j\rangle$ for $i, j \in \{x, y\}$ using $\langle\hat{S}_i\hat{S}_j\rangle$ for $i, j \in \{+, -\}$. We choose to work with these ladder operators for simplicity.

With a cGHF reference, the zeroth order expectation values are as follows:[45,46]

$$\langle \hat{S}_z \rangle_0 = \frac{1}{2}\sum_i \left(\langle i_\alpha | i_\alpha \rangle - \langle i_\beta | i_\beta \rangle\right) \tag{S15}$$

$$\langle \hat{S_+} \rangle_0 = \langle \hat{S_-} \rangle_0^* = \sum_i \langle i_\alpha | i_\beta \rangle \tag{S16}$$

$$\begin{aligned}\langle \hat{S}_z^2 \rangle_0 =& \frac{1}{4}\sum_i \left(\langle i_\alpha | i_\alpha \rangle + \langle i_\beta | i_\beta \rangle\right)\\ &+ \frac{1}{4}\sum_{ij}\sum_{\sigma\in\{\alpha,\beta\}} \left(\langle i_\sigma | i_\sigma \rangle\langle j_\sigma | j_\sigma \rangle - \langle i_\sigma | j_\sigma \rangle\langle j_\sigma | i_\sigma \rangle\right)\\ &+ \frac{1}{4}\sum_{ij} \left(\langle i_\beta | j_\beta \rangle\langle j_\alpha | i_\alpha \rangle - \langle i_\alpha | i_\alpha \rangle\langle j_\beta | j_\beta \rangle + \text{h.c.}\right)\end{aligned} \tag{S17}$$

$$\langle \hat{S}_-\hat{S}_+ \rangle_0 = \sum_i \langle i_\beta | i_\beta \rangle + \sum_{ij} \left(\langle i_\alpha | i_\beta \rangle\langle j_\beta | j_\alpha \rangle - \langle i_\beta | j_\alpha \rangle\langle j_\alpha | i_\beta \rangle\right) \tag{S18}$$

$$\langle \hat{S}_+\hat{S}_- \rangle_0 = \sum_i \langle i_\alpha | i_\alpha \rangle + \sum_{ij} \left(\langle i_\alpha | i_\beta \rangle\langle j_\beta | j_\alpha \rangle - \langle i_\beta | j_\alpha \rangle\langle j_\alpha | i_\beta \rangle\right) \tag{S19}$$

$$\langle \hat{S}_-\hat{S}_- \rangle_0 = \langle \hat{S}_+\hat{S}_+ \rangle_0^* = \sum_{ij} \left(\langle i_\beta | i_\alpha \rangle\langle j_\beta | j_\alpha \rangle - \langle j_\beta | i_\alpha \rangle\langle i_\beta | j_\alpha \rangle\right) \tag{S20}$$

$$\begin{aligned}\langle \hat{S}_+\hat{S}_z \rangle_0 = \langle \hat{S}_z\hat{S}_- \rangle_0^* =& -\frac{1}{2}\sum_i \langle i_\alpha | i_\beta \rangle + \frac{1}{2}\sum_{ij} \left(\langle i_\alpha | i_\beta \rangle\langle j_\alpha | j_\alpha \rangle - \langle j_\alpha | i_\beta \rangle\langle i_\alpha | j_\alpha \rangle\right)\\ &- \frac{1}{2}\sum_{ij} \left(\langle i_\alpha | i_\beta \rangle\langle j_\beta | j_\beta \rangle - \langle i_\beta | j_\beta \rangle\langle j_\alpha | i_\beta \rangle\right)\end{aligned} \tag{S21}$$

$$\begin{aligned}\langle \hat{S}_-\hat{S}_z \rangle_0 = \langle \hat{S}_z\hat{S}_+ \rangle_0^* =& \frac{1}{2}\sum_i \langle i_\beta | i_\alpha \rangle + \frac{1}{2}\sum_{ij} \left(\langle i_\beta | i_\alpha \rangle\langle j_\alpha | j_\alpha \rangle - \langle i_\alpha | j_\alpha \rangle\langle j_\beta | i_\alpha \rangle\right)\\ &- \frac{1}{2}\sum_{ij} \left(\langle i_\beta | i_\alpha \rangle\langle j_\beta | j_\beta \rangle - \langle i_\beta | j_\beta \rangle\langle j_\beta | i_\alpha \rangle\right)\end{aligned} \tag{S22}$$

where we used the fact that each orbital is of the spinor form in Eq. (6) and we define

$$\langle p_{\sigma_1} | q_{\sigma_2} \rangle = \int_{\mathbf{r}} (\phi_p^{\sigma_1}(\mathbf{r}))^* \phi_q^{\sigma_2}(\mathbf{r}). \tag{S23}$$

We note that there is no spin integration in Eq. (S23). These are used to compute the covariance matrix $A_{ij} = \langle \hat{S}_i\hat{S}_j \rangle - \langle \hat{S}_i \rangle\langle \hat{S}_j \rangle$. As noted before, the eigenspectrum of $\mathbf{A}$ determines whether the GHF wavefunction is genuinely non-collinear. The wavefunction is collinear if and only if there is a zero eigenmode.

Similarly, the first-order corrections to these expectation values can be obtained from

$$\langle \hat{O} \rangle_1 = \frac{1}{4} \sum_{ijab} \left(t_{ij}^{ab} \right)^* \langle \Psi_{ij}^{ab} | \hat{O} | \Psi_0 \rangle + \frac{1}{4} \sum_{ijab} \langle \Psi_0 | \hat{O} | \Psi_{ij}^{ab} \rangle t_{ij}^{ab} \tag{S24}$$

This can be easily computed as follows:

$$\langle \hat{S}_z \rangle_1 = \langle \hat{S}_+ \rangle_1 = \langle \hat{S}_- \rangle_1 = 0 \tag{S25}$$

$$\begin{aligned} \langle \hat{S}_z^2 \rangle_1 = & \frac{1}{4} \sum_{\substack{i<j \\ a<b}} \left(t_{ij}^{ab} \right)^* \sum_{\sigma \in \{\alpha, \beta\}} \left(2\langle a_\sigma | i_\sigma \rangle \langle b_\sigma | j_\sigma \rangle - 2\langle a_\sigma | j_\sigma \rangle \langle b_\sigma | i_\sigma \rangle \right) \\ & + \frac{1}{4} \sum_{\substack{i<j \\ a<b}} \left(t_{ij}^{ab} \right)^* (-2\langle a_\alpha | i_\alpha \rangle \langle b_\beta | j_\beta \rangle + 2\langle a_\beta | j_\beta \rangle \langle b_\alpha | i_\alpha \rangle \\ & - 2\langle a_\beta | i_\beta \rangle \langle b_\alpha | j_\alpha \rangle + 2\langle a_\alpha | j_\alpha \rangle \langle b_\beta | i_\beta \rangle) + \text{h.c.} \end{aligned} \tag{S26}$$

$$\begin{aligned} \langle \hat{S}_- \hat{S}_+ \rangle_1 = \langle \hat{S}_+ \hat{S}_- \rangle_1 = & \sum_{\substack{i<j \\ a<b}} (t_{ij}^{ab})^* (\langle a_\beta | i_\alpha \rangle \langle b_\alpha | j_\beta \rangle - \langle a_\alpha | j_\beta \rangle \langle b_\beta | i_\alpha \rangle \\ & + \langle a_\alpha | i_\beta \rangle \langle b_\beta | j_\alpha \rangle - \langle a_\beta | j_\alpha \rangle \langle b_\alpha | i_\beta \rangle) + \text{h.c.} \end{aligned} \tag{S27}$$

$$\begin{aligned} \langle \hat{S}_- \hat{S}_- \rangle_1 = \langle \hat{S}_+ \hat{S}_+ \rangle_1^* = & \sum_{\substack{i<j \\ a<b}} (t_{ij}^{ab})^* \left(2\langle a_\beta | i_\alpha \rangle \langle b_\beta | j_\alpha \rangle - 2\langle a_\beta | j_\alpha \rangle \langle b_\beta | i_\alpha \rangle \right) \\ & + \sum_{\substack{i<j \\ a<b}} (t_{ij}^{ab}) \left(2\langle i_\beta | a_\alpha \rangle \langle j_\beta | b_\alpha \rangle - 2\langle j_\beta | a_\alpha \rangle \langle i_\beta | b_\alpha \rangle \right) \end{aligned} \tag{S28}$$

$$\langle \hat{S}_+\hat{S}_z\rangle_1 = \langle \hat{S}_z\hat{S}_-\rangle_1^* = \frac{1}{2}\sum_{\substack{i<j\\a<b}}(t_{ij}^{ab})^*(\langle a_\alpha|i_\beta\rangle\langle b_\alpha|j_\alpha\rangle - \langle a_\alpha|j_\alpha\rangle\langle b_\alpha|i_\beta\rangle$$
$$+ \langle a_\alpha|i_\alpha\rangle\langle b_\alpha|j_\beta\rangle - \langle a_\alpha|j_\beta\rangle\langle b_\alpha|i_\alpha\rangle - \langle a_\alpha|i_\beta\rangle\langle b_\beta|j_\beta\rangle$$
$$+ \langle a_\beta|j_\beta\rangle\langle b_\alpha|i_\beta\rangle - \langle a_\beta|i_\beta\rangle\langle b_\alpha|j_\beta\rangle + \langle a_\alpha|j_\beta\rangle\langle b_\beta|i_\beta\rangle)$$
$$+ \frac{1}{2}\sum_{\substack{i<j\\a<b}} t_{ij}^{ab}(\langle i_\alpha|a_\alpha\rangle\langle j_\alpha|b_\beta\rangle - \langle j_\alpha|a_\beta\rangle\langle i_\alpha|b_\alpha\rangle$$
$$+ \langle i_\alpha|a_\beta\rangle\langle j_\alpha|b_\alpha\rangle - \langle j_\alpha|a_\alpha\rangle\langle i_\alpha|b_\beta\rangle - \langle i_\beta|a_\beta\rangle\langle j_\alpha|b_\beta\rangle$$
$$+ \langle j_\alpha|a_\beta\rangle\langle i_\beta|b_\beta\rangle - \langle i_\alpha|a_\beta\rangle\langle j_\beta|b_\beta\rangle + \langle j_\beta|a_\alpha\rangle\langle i_\alpha|b_\beta\rangle) \tag{S29}$$

$$\langle \hat{S}_-\hat{S}_z\rangle_1 = \langle \hat{S}_z\hat{S}_+\rangle_1^* = \frac{1}{2}\sum_{\substack{i<j\\a<b}}(t_{ij}^{ab})^*(\langle a_\beta|i_\alpha\rangle\langle b_\alpha|j_\alpha\rangle - \langle a_\alpha|j_\alpha\rangle\langle b_\beta|i_\alpha\rangle$$
$$+ \langle a_\alpha|i_\alpha\rangle\langle b_\beta|j_\alpha\rangle - \langle a_\beta|j_\alpha\rangle\langle b_\alpha|i_\alpha\rangle - \langle a_\beta|i_\alpha\rangle\langle b_\beta|j_\beta\rangle$$
$$+ \langle a_\beta|j_\beta\rangle\langle b_\beta|i_\alpha\rangle - \langle a_\beta|i_\beta\rangle\langle b_\beta|j_\alpha\rangle + \langle a_\beta|j_\alpha\rangle\langle b_\beta|i_\beta\rangle)$$
$$+ \frac{1}{2}\sum_{\substack{i<j\\a<b}} t_{ij}^{ab}(\langle i_\alpha|a_\alpha\rangle\langle j_\beta|b_\beta\rangle - \langle j_\beta|a_\alpha\rangle\langle i_\alpha|b_\alpha\rangle$$
$$+ \langle i_\beta|a_\alpha\rangle\langle j_\alpha|b_\alpha\rangle - \langle j_\alpha|a_\alpha\rangle\langle i_\beta|b_\alpha\rangle - \langle i_\beta|a_\beta\rangle\langle j_\beta|b_\alpha\rangle$$
$$+ \langle j_\beta|a_\alpha\rangle\langle i_\beta|b_\beta\rangle - \langle i_\beta|a_\alpha\rangle\langle j_\beta|b_\beta\rangle + \langle j_\beta|a_\beta\rangle\langle i_\beta|b_\alpha\rangle) \tag{S30}$$

Complex Generalized HF

The variation in the energy expression reads

$$\delta E = \sum_{ia}(-h_{ai}\delta\Theta_{ia} - h_{ia}\delta\Theta_{ia}^*) - \frac{1}{2}\sum_{ija}\left(\langle ij \parallel aj\rangle\,\delta\Theta_{ia}^* + \langle ij \parallel ia\rangle\,\delta\Theta_{ja}^* + \langle aj \parallel ij\rangle\,\delta\Theta_{ia} + \langle ia \parallel ij\rangle\,\delta\Theta_{ja}\right)$$

where $\delta\Theta_{ia}$ is an infinitesimal orbital rotation. This energy variation can be used to compute orbital gradient and similarly orbital hessian.

Orbital Gradient

We compute the gradient of E with respect to the real and imaginary part of $\mathbf{\Theta}$,

$$\frac{\partial E}{\partial \mathrm{Re}(\Theta_{ia})} = -\left[h_{ai} + J_{ai} - K_{ai}\right] + \text{h.c.} = -h_{ai} - \sum_k \langle ak||ik\rangle - h_{ia} - \sum_k \langle ik||ak\rangle$$

$$\frac{\partial E}{\partial i\mathrm{Im}(\Theta_{ia})} = -\left[h_{ai} + J_{ai} - K_{ai}\right] - \text{h.c.} = -h_{ai} - \sum_k \langle ak||ik\rangle + h_{ia} + \sum_k \langle ik||ak\rangle$$

Orbital Hessian

Similarly, the variation of orbital gradient reads

$$\delta\frac{\partial E}{\partial \mathrm{Re}(\Theta_{ia})} = \sum_j \left(-h_{ji}\delta\Theta^*_{ja} + h_{ab}\delta\Theta^*_{bi}\right) + \sum_k \left(-\sum_j \delta\Theta^*_{aj}\langle jk||ik\rangle + \sum_b \delta\Theta^*_{bi}\langle ak||bk\rangle\right) + \sum_{kb} \delta\Theta^*_{bk}\langle ak||ib\rangle + \sum_{kb} \delta\Theta_{bk}\langle ab||ik\rangle + \text{h.c.} \tag{S31}$$

and

$$\delta\frac{\partial E}{\partial i\mathrm{Im}(\Theta_{ia})} = \sum_j \left(-h_{ji}\delta\Theta^*_{ja} + h_{ab}\delta\Theta^*_{bi}\right) + \sum_k \left(-\sum_j \delta\Theta^*_{aj}\langle jk||ik\rangle + \sum_b \delta\Theta^*_{bi}\langle ak||bk\rangle\right) + \sum_{kb} \delta\Theta^*_{bk}\langle ak||ib\rangle + \sum_{kb} \delta\Theta_{bk}\langle ab||ik\rangle - \text{h.c.} \tag{S32}$$

These are then used to obtain orbital hessian:

$$\frac{\partial^2 E}{\partial \mathrm{Re}(\Theta_{ia})\partial \mathrm{Re}(\Theta_{jb})} = \left[-\delta_{ab}\left(h_{ji} + \sum_k \langle jk||ik\rangle\right) + \delta_{ij}\left(h_{ab} + \sum_k \langle ak||bk\rangle\right) + \langle aj||ib\rangle + \langle ab||ij\rangle\right] + h.c \tag{S33}$$

$$\frac{\partial^2 E}{\partial i \mathrm{Im}(\Theta_{ia}) \partial i \mathrm{Im}(\Theta_{jb})} = \left[\delta_{ab}\left(h_{ji} + \sum_k \langle jk||ik\rangle\right) - \delta_{ij}\left(h_{ab} + \sum_k \langle ak||bk\rangle\right) - \langle aj||ib\rangle + \langle ab||ij\rangle\right] + h.c$$
$$= -\frac{\partial^2 E}{\partial \mathrm{Im}(\Theta_{ia}) \partial \mathrm{Im}(\Theta_{jb})} \tag{S34}$$

$$\frac{\partial^2 E}{\partial \mathrm{Im}(\Theta_{ia}) \partial \mathrm{Re}(\Theta_{jb})} = i\left[-\langle aj||ib\rangle + \langle ab||ij\rangle - h.c.\right] \tag{S35}$$

$$\frac{\partial^2 E}{\partial \mathrm{Re}(\Theta_{ia}) \partial \mathrm{Im}(\Theta_{jb})} = -\, i\left[-\langle aj||ib\rangle + \langle ab||ij\rangle - h.c.\right] \tag{S36}$$