Excited States, Symmetry Breaking, and Unphysical Solutions in State-Specific CASSCF Theory: Supporting Information

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S1. Deriving the gradient and second-derivative of the CASSCF energy

S1.1. Notation and reduced density matrices

Here, we provide explicit expressions for the gradient and Hessian of the CASSCF energy, which are required for quasi-Newton optimisation algorithms. These expressions are derived in detail in Refs. 1 and 2, but we include this pedagogical discussion for completeness. In what follows, the indices m, n, p, q, r, s correspond to arbitrary spatial orbitals, i, j, k, l correspond to occupied orbitals, a, b, c, d correspond to virtual orbitals, and t, v, x, y correspond to active orbitals. Furthermore, we employ the ground-state one- and two-body reduced densities,

$$\gamma_{pq} = \sum_{\sigma} \langle \Psi_0 | \hat{a}_{q\sigma}^{\dagger} \hat{a}_{p\sigma} | \Psi_0 \rangle, \tag{S1a}$$

$$\Gamma_{pqrs} = \sum_{\sigma\tau} \langle \Psi_0 | \hat{a}_{p\sigma}^{\dagger} \hat{a}_{r\tau}^{\dagger} \hat{a}_{s\tau} \hat{a}_{q\sigma} | \Psi_0 \rangle, \tag{S1b}$$

and the transition density matrices

$$\gamma_{pq}^{K} = \sum_{\sigma} \langle \Psi_0 | \hat{a}_{q\sigma}^{\dagger} \hat{a}_{p\sigma} | \Psi_K \rangle, \tag{S2a}$$

$$\Gamma_{pqrs}^{K} = \sum_{\sigma\tau} \langle \Psi_0 | \hat{a}_{p\sigma}^{\dagger} \hat{a}_{r\tau}^{\dagger} \hat{a}_{s\tau} \hat{a}_{q\sigma} | \Psi_K \rangle. \tag{S2b}$$

Explicit expressions for the non-zero matrix elements can be simplified depending on the types of orbitals involved, giving expressions for the ground-state density matrices as

$$\gamma_{ij} = 2\delta_{ij} \tag{S3}$$

and

$$\Gamma_{ijkl} = 4\delta_{ij}\delta_{kl} - 2\delta_{il}\delta_{kj}, \qquad \Gamma_{ijtv} = 2\delta_{ij}\gamma_{vt}, \qquad \text{and} \qquad \Gamma_{ivtj} = -\delta_{ij}\gamma_{vt}. \tag{S4}$$

where the purely active components γ_{tv} and Γ_{tvxy} cannot be simplified beyond Eq. S1. The only non-zero component of the one-body transition density matrix is γ_{tv}^{K}. In addition to the Γ_{tvxy}^{K} components, the non-zero terms of the two-body transition density matrix include

$$\Gamma_{ijtv}^{K} = 2\delta_{ij}\gamma_{vt}^{K}, \qquad \text{and} \qquad \Gamma_{ivtj}^{K} = -\delta_{ij}\gamma_{vt}^{K}. \tag{S5}$$

S1.2. Gradient terms

The gradient can be divided into the orbital components g^{o} and the CI components g^{c} that are defined in the main text. The CI components are given by the Hamiltonian matrix elements in the configuration space, that is

$$g_K^{\text{c}} = 2\langle \Psi_0 | \hat{H} | \Psi_K \rangle. \tag{S6}$$

The orbital components are given by

$$g_{mn}^{\text{o}} = \langle \Psi_0 | [\hat{H}, \hat{E}_{mn}^{-}] | \Psi_0 \rangle \tag{S7}$$

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where

$$\langle\Psi_0|[\hat{H},\hat{E}_{mn}]|\Psi_0\rangle = \sum_p \left(h_{mp}\gamma_{pn} + \gamma_{np}h_{pm}\right) + \sum_{prs}\left[(pm|rs)\Gamma_{pnrs} + (mp|rs)\Gamma_{nprs}\right], \tag{S8}$$

and we have introduced the singlet excitation operator

$$\hat{E}_{mn} = \sum_{\sigma\in\{\uparrow,\downarrow\}} \hat{a}^\dagger_{m\sigma}\hat{a}_{n\sigma} \tag{S9}$$

with its anti-symmetrized variant $\hat{E}^-_{mn} = \hat{E}_{mn} - \hat{E}_{nm}$.

S1.3. Hessian terms

Similarly, we can divide the Hessian $\boldsymbol{Q}$ into three components: $\boldsymbol{Q}^{\text{cc}}$, $\boldsymbol{Q}^{\text{oo}}$ and $\boldsymbol{Q}^{\text{oc}}$ (where $H^{\text{co}} = (\boldsymbol{Q}^{\text{oc}})^\dagger$). The CI-CI components are given by the Hamiltonian matrix elements within the active configuration space shifted by the current energy E_0, giving

$$Q^{\text{cc}}_{K,L} = 2\langle\Psi_K|\hat{H} - E_0|\Psi_L\rangle. \tag{S10}$$

The off-diagonal components corresponding to the orbital-CI matrix elements are given by

$$Q^{\text{oc}}_{mn,K} = \langle\Psi_0|[\hat{H},\hat{E}^-_{mn}]|\Psi_K\rangle \tag{S11}$$

where the constituent transition matrix elements are computed as

$$\langle\Psi_K|[\hat{H},\hat{E}_{mn}]|\Psi_0\rangle = \sum_p \left(h_{mp}\gamma^K_{pn} + \gamma^K_{np}h_{pm}\right) + \sum_{prs}\left[(pm|rs)\Gamma^K_{pnrs} + (mp|rs)\Gamma^K_{nprs}\right]. \tag{S12}$$

The final orbital-orbital term is given by

$$Q^{\text{oo}}_{pq,rs} = \frac{1}{2}\left(\langle\Psi_0|[[\hat{H},\hat{E}^-_{pq}],\hat{E}^-_{rs}]|\Psi_0\rangle + \langle\Psi_0|[[\hat{H},\hat{E}^-_{rs}],\hat{E}^-_{pq}]|\Psi_0\rangle\right). \tag{S13}$$

While a full derivation using the results of Ref. 2 is lengthy, the non-redundant blocks are:

- Virtual-Core, Virtual-Core:

$$Q^{\text{oo}}_{ai,bj} = 4[4(ai|bj) - (ab|ij) - (aj|bi)] + 4\delta_{ij}(F^{\text{C}}_{ab} + F^{\text{A}}_{ab}) - 4\delta_{ab}(F^{\text{C}}_{ij} + F^{\text{A}}_{ij}) \tag{S14}$$

- Virtual-Core, Virtual-Active:

$$Q^{\text{oo}}_{ai,bt} = 2\sum_v \gamma_{tv}[4(ai|bv) - (av|bi) - (ab|vi)] - \delta_{ab}\left(\sum_v \gamma_{tv}F^{\text{C}}_{iv} + 2(F^{\text{C}}_{ti} + F^{\text{A}}_{ti}) + \sum_{vxy}\Gamma_{tvxy}(vi|xy)\right) \tag{S15}$$

- Virtual-Core, Active-Core:

$$Q^{\text{oo}}_{ai,tj} = 2\sum_v (2\delta_{tv} - \gamma_{tv})[4(ai|vj) - (av|ji) - (aj|vi)] - \delta_{ij}\left(\sum_v \gamma_{tv}F^{\text{C}}_{av} - 4(F^{\text{C}}_{at} + F^{\text{A}}_{at}) + \sum_{vxy}\Gamma_{tvxy}(av|xy)\right) \tag{S16}$$

- Virtual-Active, Virtual-Active:

$$Q^{\text{oo}}_{at,bu} = 2\sum_{vx}\left(\Gamma_{tuvx}(ab|vx) + (\Gamma_{txvu} + \Gamma_{txuv})(ax|bv)\right) - \delta_{ab}\left(\sum_v\left(\gamma_{tv}F^{\text{C}}_{uv} + \gamma_{uv}F^{\text{C}}_{tv}\right) + \sum_{vxy}\left(\Gamma_{tvxy}(uv|xy) + \Gamma_{uvxy}(tv|xy)\right)\right) + 2\gamma_{tu}F^{\text{C}}_{ab} \tag{S17}$$

- Active-Core, Virtual-Active:

$$Q^{\text{oo}}_{ti,au} = -2\sum_{vx}\left(\Gamma_{tuvx}(ai|vx) + (\Gamma_{tvux} + \Gamma_{tvxu})(ax|vi)\right) + 2\sum_v \gamma_{uv}\left(4(av|ti) - (ai|tv) - (at|vi)\right) - 2\gamma_{tu}F^{\text{C}}_{ia} + \delta_{tu}(F^{\text{C}}_{ai} + F^{\text{A}}_{ai}) \tag{S18}$$

- Active-Core, Active-Core:

$$G_{ti,uj} = 4 \sum_{v} (\delta_{tv} - \gamma_{tv}) \Big(4(vi|uj) - (ui|vj) - (uv|ij) \Big) + 2 \sum_{vx} \Big(\Gamma_{utvx}(vx|ij) + (\Gamma_{uxvt} + \Gamma_{uxtv})(vi|xj) \Big)$$

$$+ 2\gamma_{tu}F_{ij}^{C} - 2\delta_{ij} \Big(\sum_{vxy} \Gamma_{tvxy}(uv|xy) + \sum_{v} \gamma_{uv}F_{tv}^{C} \Big) + 4\delta_{ij}(F_{tu}^{C} + F_{tu}^{A}) - 4\delta_{tu}(F_{ij}^{C} + F_{ij}^{A}) \tag{S19}$$

$$Q_{ti,uj}^{\mathrm{oo}} = \frac{1}{2}\Big(G_{ti,uj} + G_{uj,ti}\Big).$$

Here, we have introduced the inactive (core) and active Fock matrices[2]

$$F_{mn}^{C} = h_{mn} + \sum_{i} [2(mn|ii) - (mi|in)] \qquad \text{and} \qquad F_{mn}^{A} = \sum_{tv} \gamma_{tv}[(mn|tv) - \frac{1}{2}(mv|tn)]. \tag{S20}$$

S2. Eigenvector-following for saddle point optimisation

We employ the eigenvector-following technique to target stationary points with an arbitrary Hessian index. While Section 6.2.1 of Ref. [3], and references therein, describe this method in detail, here we summarise the salient points for completeness and provide the details of our particular implementation.

Eigenvector-following works in the eigenbasis for the Hessian matrix Q with eigenvalues ϵ_μ. In this basis, the components of the Newton–Raphson step $x = -Q^{-1}g$, with gradient g, and the change in energy ΔV are given by

$$x_{\mathrm{NR},\mu} = -\frac{g_\mu}{\epsilon_\mu} \qquad \text{and} \qquad \Delta V_{\mathrm{NR}} = -\sum_\mu \frac{|g_\mu|^2}{2\epsilon_\mu}. \tag{S21}$$

Contributions with $\epsilon_\mu > 0$ or $\epsilon_\mu < 0$ lower or raise the energy, respectively. To drive the optimisation towards a particular type of Hessian index, eigenvector-following artificially modifies the sign of these components. In particular, the components of the quasi-Newton eigenvector-following step are defined as

$$x_{\mathrm{QN},\mu} = \frac{\pm 2g_\mu}{|\epsilon_\mu|\left(1 + \sqrt{1 + |2g_\mu/\epsilon_\mu|^2}\right)}, \tag{S22}$$

where a positive or negative step gives an uphill or downhill step, respectively. This expression reduces to the Newton–Raphson step in the $g_\mu \to 0$ limit and can be understood by imposing constraints on each component using Lagrange multipliers.[3] When an index-n saddle point is targeted in this work, the components corresponding to the lowest n eigenvalues of the Hessian are chosen to be downhill directions.

Furthermore, we employ a dogleg trust radius technique to control the step length and improve the local convergence behaviour. A trust radius method works by defining a region with radius ρ around the current point in which a quadratic approximation to the objective function is considered to be accurate. The next step is chosen by optimising the objective function within this trust region, known as the sub-problem. In practice, approximate solutions to the sub-problem are required, and we employ the dogleg method (see Section 4.1 of Ref. [4]). This method requires an analogue of the steepest descent direction for saddle point optimisation, which we define as

$$x_{\mathrm{SD},\mu} = \pm g_\mu, \tag{S23}$$

where the positive and negative sign for each component are chosen in the same way as the quasi-Newton step [Eq. (S22)]. Defining an unconstrained step which optimises the energy along the steepest descent direction as

$$x_{\mathrm{U}} = -\frac{g^\dagger x_{\mathrm{SD}}}{x_{\mathrm{SD}}^\dagger Q x_{\mathrm{SD}}} x_{\mathrm{SD}}, \tag{S24}$$

and using the eigenvector-following quasi-Newton step x_{QN}, the optimal dogleg step x is then given by

$$x = \begin{cases} x_{\mathrm{QN}} & \text{if } |x_{\mathrm{QN}}| \le \rho \\ \frac{\rho}{|x_{\mathrm{U}}|} x_{\mathrm{U}} & \text{if } |x_{\mathrm{U}}| \ge \rho \\ x_{\mathrm{U}} + \tau\,(x_{\mathrm{QN}} - x_{\mathrm{U}}) & \text{otherwise} \end{cases} \tag{S25}$$

where

$$\tau = \frac{-b + \sqrt{b^2 - 4ac}}{2a}, \qquad a = \left|\boldsymbol{x}_{\text{QN}} - \boldsymbol{x}_{\text{U}}\right|^2, \qquad b = 2\boldsymbol{x}_{\text{U}} \cdot (\boldsymbol{x}_{\text{QN}} - \boldsymbol{x}_{\text{U}}), \qquad c = |\boldsymbol{x}_{\text{U}}|^2 - \rho^2. \tag{S26}$$

The trust radius is then updated by comparing the ratio of the actual energy change ΔE to that predicted by the quadratic model ΔE_{model}. The trust radius is halved for $\Delta E / \Delta E_{\text{model}} < 0.25$, and doubled if $\Delta E / \Delta E_{\text{model}} > 0.75$ and $|\boldsymbol{x}_{\text{DL}}| = \rho$. Otherwise, the trust radius is not deemed to be interfering with the optimisation and is left unchanged. Finally, a step is rejected if ΔE and ΔE_{model} have different signs. We find that an initial trust radius of 0.15 provides adequate optimisation behaviour.

S3. Mode-controlled Newton–Raphson optimisation

Once a stationary point has been identified, it can be followed along a potential energy surface by using the old orbital and CI coefficients as a guess at the new geometry. Since the Hessian index can change at different geometries, we use a standard Newton–Raphson optimisation to perform this optimisation. The Newton–Raphson step is identified by solving a quadratic Taylor series expansion to the energy around a given point, giving

$$\boldsymbol{x}_{\text{NR}} = -\boldsymbol{Q}^{-1}\boldsymbol{g} \tag{S27}$$

for the gradient $\boldsymbol{g}$ and Hessian matrix of second derivatives $\boldsymbol{Q}$. The dogleg method (described in Section S2) cannot be used as there is no way of defining a "steepest descent" step for saddle point optimisation without knowing the target Hessian index. Instead, we simply truncate the components of $\boldsymbol{x}_{\text{NR}}$ depending on their magnitude along each eigen-direction of the $\boldsymbol{Q}$, giving

$$x_\mu = \min\left(|x_{\text{NR},\mu}|, \rho\right) \frac{x_{\text{NR},\mu}}{|x_{\text{NR},\mu}|}. \tag{S28}$$

The trust radius ρ is then updated using the same strategy described in Section S2. Similar mode-controlled Newton–Raphson optimisation algorithms have been reported multiple times in the past.[1,5–7]

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