Exercises on second quantization and MCSCF

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1 Generalized Brillouin theorem

Like in standard (non-relativistic) quantum chemistry, *real algebra* will be used throughout the exercise, for simplicity. We focus on the orbital optimization in the MCSCF wave function that can be parameterized as follows, $\left|\Psi^{\rm MC}(\boldsymbol{\kappa})\right\rangle = e^{-\hat{\kappa}}\left|\Psi_0^{\rm MC}\right\rangle$, where $\Psi_0^{\rm MC}$ is a normalized multiconfigurational wave function, $\boldsymbol{\kappa} \equiv \{\kappa_{PQ}\}_{P<Q}$ the collection of real spin-orbital rotation parameters, and $\hat{\kappa} = \sum_{P<Q} \kappa_{PQ}\left(\hat{a}_P^\dagger \hat{a}_Q - \hat{a}_Q^\dagger \hat{a}_P\right)$ is the anti-hermitian operator that controls orbital rotations in second quantization.

a) Show that, if $\Psi_0^{\rm MC}$ is the converged (energy-minimizing) MCSCF wave function, then the following stationarity condition is fulfilled,

$$0 = \left.\frac{\partial \left\langle \Psi^{\rm MC}(\boldsymbol{\kappa})\middle|\hat{H}\middle|\Psi^{\rm MC}(\boldsymbol{\kappa})\right\rangle}{\partial \kappa_{PQ}}\right|_{\boldsymbol{\kappa}=0} = 2\left\langle \Psi_0^{\rm MC}\middle|\left[\hat{a}_P^\dagger \hat{a}_Q, \hat{H}\right]\middle|\Psi_0^{\rm MC}\right\rangle \quad (1)$$

$$= 2\left(\left\langle \Psi_0^{\rm MC}\middle|\hat{H}\hat{a}_Q^\dagger \hat{a}_P\middle|\Psi_0^{\rm MC}\right\rangle - \left\langle \Psi_0^{\rm MC}\middle|\hat{H}\hat{a}_P^\dagger \hat{a}_Q\middle|\Psi_0^{\rm MC}\right\rangle\right) = 0, \quad (2)$$

which is known as generalized Brillouin theorem. The purpose of the exercise is to explain the name of the theorem and establish a clearer connection between Eq. (2) and the Fock operator that is diagonalized in the Hartree–Fock method.

b) Show that if, for example, $Q = A$ and $P = I$ are virtual (unoccupied in $\Psi_0^{\rm MC}$) and inactive (always occupied in $\Psi_0^{\rm MC}$) spin-orbitals, respectively, then Eq. (2) simply reads $\left\langle \Psi_0^{\rm MC}\middle|\hat{H}\hat{a}_A^\dagger \hat{a}_I\middle|\Psi_0^{\rm MC}\right\rangle = 0$. Why do we refer to Eq. (2) as *generalized* Brillouin theorem?

Comment: If $P = I$ and $Q = U$ is an active spin-orbital then $\hat{a}_P^\dagger \hat{a}_Q\left|\Psi_0^{\rm MC}\right\rangle = -\hat{a}_U \hat{a}_I^\dagger\left|\Psi_0^{\rm MC}\right\rangle = 0$ and therefore $\left\langle \Psi_0^{\rm MC}\middle|\hat{H}\hat{a}_U^\dagger \hat{a}_I\middle|\Psi_0^{\rm MC}\right\rangle = 0$.
If $P = U$ and $Q = A$ then $\hat{a}_P^\dagger \hat{a}_Q\left|\Psi_0^{\rm MC}\right\rangle = \hat{a}_U^\dagger \hat{a}_A\left|\Psi_0^{\rm MC}\right\rangle = 0$ and therefore $\left\langle \Psi_0^{\rm MC}\middle|\hat{H}\hat{a}_A^\dagger \hat{a}_U\middle|\Psi_0^{\rm MC}\right\rangle = 0$.

2 Commutators of strings of creation and annihilation operators

a) Verify the relations

$$\left[\hat{A}, \hat{B} + \hat{C}\right] = \left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{C}\right] \quad (3)$$

and

$$\left[\hat{A},\hat{B}\right]\hat{C}+\hat{B}\left[\hat{A},\hat{C}\right]=\left[\hat{A},\hat{B}\right]_{+}\hat{C}-\hat{B}\left[\hat{A},\hat{C}\right]_{+}=\left[\hat{A},\hat{B}\hat{C}\right], \tag{4}$$

where $\left[\hat{A},\hat{B}\right]=\hat{A}\hat{B}-\hat{B}\hat{A}$ and $\left[\hat{A},\hat{B}\right]_{+}=\hat{A}\hat{B}+\hat{B}\hat{A}$ are the commutator and anti-commutator operators of $\hat{A}$ and $\hat{B}$, respectively.

b) Evaluate the anti-commutators $[\hat{a}_I,\hat{a}_J]_+$, $\left[\hat{a}_I^\dagger,\hat{a}_J^\dagger\right]_+$, and $\left[\hat{a}_I^\dagger,\hat{a}_J\right]_+$ by applying the rules of second quantization.

c) Explain the following simplifications on the basis of Eq. 4)

$$\begin{aligned}
[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\hat{a}_L] &= \left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\right]\hat{a}_L+\hat{a}_K^\dagger\left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_L\right] &(5)\\
&= -\left[\hat{a}_K^\dagger,\hat{a}_I^\dagger\hat{a}_J\right]\hat{a}_L-\hat{a}_K^\dagger\left[\hat{a}_L,\hat{a}_I^\dagger\hat{a}_J\right] &(6)\\
&= -\left[\hat{a}_K^\dagger,\hat{a}_I^\dagger\right]_+\hat{a}_J\hat{a}_L+\hat{a}_I^\dagger\left[\hat{a}_K^\dagger,\hat{a}_J\right]_+\hat{a}_L-\hat{a}_K^\dagger\left[\hat{a}_L,\hat{a}_I^\dagger\right]_+\hat{a}_J+\hat{a}_K^\dagger\hat{a}_I^\dagger\left[\hat{a}_L,\hat{a}_J\right]_+. &(7)
\end{aligned}$$

d) Deduce from question 1. b) that

$$[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\hat{a}_L]=\delta_{JK}\;\hat{a}_I^\dagger\hat{a}_L-\delta_{IL}\;\hat{a}_K^\dagger\hat{a}_J. \tag{8}$$

e) Similarly, show step by step that

$$\begin{aligned}
\left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\hat{a}_M\right] &= \left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\right]\hat{a}_M+\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_M\right] &(9)\\
&= \left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\hat{a}_L^\dagger\right]\hat{a}_N\hat{a}_M-\hat{a}_K^\dagger\hat{a}_L^\dagger\left[\hat{a}_N,\hat{a}_I^\dagger\hat{a}_J\right]\hat{a}_M-\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\left[\hat{a}_M,\hat{a}_I^\dagger\hat{a}_J\right] &(10)\\
&= -\left[\hat{a}_K^\dagger,\hat{a}_I^\dagger\hat{a}_J\right]\hat{a}_L^\dagger\hat{a}_N\hat{a}_M-\hat{a}_K^\dagger\left[\hat{a}_L^\dagger,\hat{a}_I^\dagger\hat{a}_J\right]\hat{a}_N\hat{a}_M\\
&\quad -\hat{a}_K^\dagger\hat{a}_L^\dagger\left[\hat{a}_N,\hat{a}_I^\dagger\hat{a}_J\right]\hat{a}_M-\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\left[\hat{a}_M,\hat{a}_I^\dagger\hat{a}_J\right], &(11)
\end{aligned}$$

and conclude, by analogy with question 1. c), that

$$\left[\hat{a}_I^\dagger\hat{a}_J,\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\hat{a}_M\right]=\delta_{JK}\;\hat{a}_I^\dagger\hat{a}_L^\dagger\hat{a}_N\hat{a}_M+\delta_{JL}\;\hat{a}_K^\dagger\hat{a}_I^\dagger\hat{a}_N\hat{a}_M-\delta_{IN}\;\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_J\hat{a}_M-\delta_{IM}\;\hat{a}_K^\dagger\hat{a}_L^\dagger\hat{a}_N\hat{a}_J. \tag{12}$$

3 Generalized Fock matrix

The purpose of this exercise is to make the stationarity condition of Eq. (1) more explicit.

a) From the second-quantized expression of the Hamiltonian,

$$\hat{H} = \sum_{KL} h_{KL} \hat{a}_K^\dagger \hat{a}_L + \frac{1}{2} \sum_{KLMN} \langle KL|MN \rangle \hat{a}_K^\dagger \hat{a}_L^\dagger \hat{a}_N \hat{a}_M, \tag{13}$$

where

$$h_{KL} = \int dX \varphi_K(X) \hat{h} \varphi_L(X) \text{ and } \langle KL|MN \rangle = \int dX_1 \int dX_2 \frac{\varphi_K(X_1)\varphi_L(X_2)\varphi_M(X_1)\varphi_N(X_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \tag{14}$$

show that, according to Eqs. (3), (8), (12), and (1),

$$\begin{aligned} &\sum_{KL} h_{KL} \left(\delta_{QK}\, \gamma_{PL} - \delta_{PL} \gamma_{KQ}\right) \\ &+ \frac{1}{2} \sum_{KLMN} \langle KL|MN \rangle \left(\delta_{QK} \Gamma_{PLNM} + \delta_{QL} \Gamma_{KPNM} - \delta_{PN} \Gamma_{KLQM} - \delta_{PM} \Gamma_{KLNQ}\right) = 0, \end{aligned} \tag{15}$$

or, equivalently,

$$F_{QP} - F_{PQ} = 0, \;\; \forall P < Q, \tag{16}$$

where

$$F_{PQ} = \sum_{L} h_{PL} \gamma_{LQ} + \sum_{LMN} \langle PL|MN \rangle \Gamma_{QLNM} \tag{17}$$

is referred to as generalized Fock matrix element,

$$\gamma_{PQ} = \left\langle \Psi_0^{\mathrm{MC}} \middle| \hat{a}_P^\dagger \hat{a}_Q \middle| \Psi_0^{\mathrm{MC}} \right\rangle \tag{18}$$

and

$$\Gamma_{PQRS} = \left\langle \Psi_0^{\mathrm{MC}} \middle| \hat{a}_P^\dagger \hat{a}_Q^\dagger \hat{a}_R \hat{a}_S \middle| \Psi_0^{\mathrm{MC}} \right\rangle \tag{19}$$

are the one- and two-electron reduced density matrix elements, respectively.

Hints: Note that

$$h_{LP} = h^*_{LP} = h_{PL}, \gamma_{PL} = \gamma^*_{PL} = \gamma_{LP}, \tag{20}$$

$$\langle KQ|MN\rangle = \langle QK|NM\rangle, \Gamma_{KPNM} = \Gamma_{PKMN}, \tag{21}$$

$$\langle KL|MP\rangle = \langle MP|KL\rangle = \langle PM|LK\rangle, \Gamma_{KLQM} = \Gamma^*_{KLQM} = \Gamma_{MQLK} = \Gamma_{QMKL}, \tag{22}$$

$$\langle KL|PN\rangle = \langle PN|KL\rangle, \Gamma_{KLNQ} = \Gamma^*_{KLNQ} = \Gamma_{QNLK}. \tag{23}$$

b) HF equations can be recovered within the present MCSCF formalism by using a single determinantal wave function rather than a multiconfigurational one:

$$\left|\Psi_0^{\text{MC}}\right\rangle \rightarrow \left|\Phi_0^{\text{HF}}\right\rangle = \prod_I^{\text{occ.}} \hat{a}_I^\dagger \left|\text{vac}\right\rangle. \tag{24}$$

Explain why, in this case, γ_{PQ} and Γ_{PQRS} are non-zero only if P, Q, R, and S are all occupied spin-orbitals (that we denote I, J, K, or L) with

$$\gamma_{IJ} = \delta_{IJ} \text{ and } \Gamma_{IJKL} = \gamma_{JK}\gamma_{IL} - \gamma_{JL}\gamma_{IK}. \tag{25}$$

c) Deduce from Eqs. (17) and (25) that, in this case, Eq. (16) simply reads

$$f_{AI} = 0, \tag{26}$$

where

$$f_{AI} = h_{AI} + \sum_J^{\text{occ.}} \Big(\langle AJ|IJ\rangle - \langle AJ|JI\rangle\Big) \equiv \langle\varphi_A|\hat{f}|\varphi_I\rangle \tag{27}$$

and A denotes a virtual (unoccupied) spin-orbital in Φ_0^{HF}. Is Eq. (26) consistent with the diagonalization of the regular Fock matrix that is performed in HF calculations?