Orthogonally Constrained Orbital Optimization: assessing changes of optimal orbitals for orthogonal multi-reference states

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Abstract

The choice of molecular orbitals is decisive in configuration interaction calculations. In this letter, a democratic description of the ground and excited states follows an orthogonally constrained orbitals optimization to produce state-specific orbitals. The approach faithfully recovers the excitation energy of a four-electron Hubbard trimer, whereas state-average calculations can miss the value by a factor 2.5. The method emphasises the need for orbitals optimization to reduce expansions and to reach spectroscopic accuracy.

Introduction

Electron transfer reactions are determinant in many different fields, ranging from biophysical processes to artificial compounds with potential applications. Ever since the synthesis of the emblematic Creutz-Taube compound\textsuperscript{1}, molecular chemistry has produced a wealth of compounds, combining different redox centers and linkers. In this context, mixed-valence inorganic compounds are excellent model systems to investigate such phenomenon. The valences can be either trapped, interconvertible with a low activation barrier, or completely delocalized. An intense intervalence charge transfer band characterizes the last categories, and magnetic exchange couplings can be observed.

Accurate methods of investigation are desirable to accurately determine band shapes and transition energies. Regardless their computational costs, the objectives are two-fold. First, spectroscopic accuracy is a prerequisite to validate their robustness and deliver means of interpretations of experimental observations. Then, the microscopic information available in the ground and excited states is a valuable contribution to rationalize the leading phenomena and to construct model Hamiltonians. From variational methods, the ground state $|\Psi_0\rangle$ can be determined using different strategies (wavefunction theory (WFT) or density functional theory (DFT)). The construction of excited states $|\Psi_I\rangle$ is much more problematic, in particular when $|\Psi_0\rangle$ and $|\Psi_I\rangle$ share the same spin and space symmetries. Even though stationary points of the expectation value of the Hamiltonian give access to excited states (Ritz’s theorem), the strategy and its implementation are not straightforward. As a major breakthrough, the maximum overlap method was designed to converge on higher solutions of the self-consistent field (SCF) equation\textsuperscript{2,3}. Despite the loss of orthogonality between the SCF solutions, the method has produced a wealth of excitation energies in different compounds\textsuperscript{2}. The key role of the molecular orbitals (MOs) in describing electron transfer processes was also stressed for the intervalence charge transfer of a synthetic nonheme binuclear mixed-valence...
compound. More recently, selected configuration interaction (CI) calculations (e.g., Configuration Interaction using a Perturbative Selection made Iteratively, CIPSI) and quantum Monte Carlo simulations were performed based on the “largest technically-affordable number of determinants” constructed on common set of natural orbitals (i.e., state-average). Excellent agreement with high-level coupled cluster references was reached in the determination of excitation energies. Tremendous efforts are still put into benchmarking multi-reference excitation energies using state-average methods and the active space selection issue.

An alternative is the application of the variational method restricted to a sub-space orthogonal to the ground state. Following this strategy, one would like to express all states on the same footing, moving away from the state-average strategy. Therefore, we designed a method here-referred to as orthogonally constrained orbital optimization (OCOO) to generate the first excited state constructed on optimized MOs and maintaining the orthogonality with the ground state. The method does not rely on any pre-conditioned structure of the excited states and somewhat differ from previous strategies. Our main intention is to identify the regimes where the MOs of the excited state strongly differ from the ground state ones. The method is applied to a three-site Hubbard Hamiltonian controlled by the on-site (\( \mu \)), hopping (\( t \)) and repulsion (\( U \)) energies (as illustrated in Figure 1).

\[
\phi_p(\kappa) = \sum_l \phi_{l}^{\text{HF}} \left[ \exp(-\kappa) \right]_{lp},
\]

\( \kappa \) being the anti-hermitian matrix generator encoding the orbital rotation parameters, and \( \{ \phi_{l}^{\text{HF}} \} \) a set of initial MOs to be optimized (in our case, Hartree-Fock MOs).

In this section, we provide the details of the OCOO to describe excited states. The method starts with the construction of a multi-reference ground state in a given model active space. The latter is constructed on a restricted number of Slater determinants built on orthogonal MOs. The expansion amplitudes and the MOs coefficients are optimized following a complete active space self-consistent field (CASSCF) framework. At convergence, an approximated ground state \( |\Psi_0^{\text{CASSCF}}\rangle \) with energy \( E_0^{\text{CASSCF}} \) is generated with an optimized MOs basis set \( B_0 \) characterized by \( \kappa_0 \). Here, “\( \kappa_0 \)” relates to the way the MOs \( |\phi_p(\kappa)\rangle \) are parametrized during the orbital optimization process:

\[
|\Psi_0^{\text{CASSCF}}\rangle = \sum_l |\phi_{l}^{\text{HF}}\rangle \left[ \exp(-\kappa) \right]_{lp},
\]

\( \kappa \) being the anti-hermitian matrix generator encoding the orbital rotation parameters, and \( \{ \phi_{l}^{\text{HF}} \} \) a set of initial MOs to be optimized (in our case, Hartree-Fock MOs).

Then, the first excited state \( |\Psi_1^{\text{OCOO}}\rangle \) is constructed with the twofold objective that is (i) to preserve orthogonality with the ground state (i.e., \( \langle \Psi_0^{\text{CASSCF}} | \Psi_1^{\text{OCOO}} \rangle = 0 \)), and (ii) to optimize the MOs to generate a state-specific \( B_1 \) basis set (\( \kappa = \kappa_1 \)). In practice, it is assumed that the multi-reference structure of both \( |\Psi_1^{\text{OCOO}}\rangle \) and \( |\Psi_0^{\text{CASSCF}}\rangle \) follow the same level of description. These states are built with the same number of “active-space like” Slater determinants in their respective optimized basis sets \( B_0 \) and \( B_1 \). Therefore, any basis set modification is likely to change the physical content of the four configurations. Let us stress that no assumption on the excited state structure is made here, in contrast with strategies used in some reported WFT- and DFT-based approaches (see Refs. 2,11,13). How do the basis \( B_0 \) and \( B_1 \) differ is at the heart of the present study.

In practice, the first excited state energy is

Figure 1: Illustration of the model systems ruled by a Hubbard Hamiltonian.
estimated by solving the effective eigenvalue problem with fixed parameter $\kappa^*$:

$$\hat{P}(\kappa^*) \hat{H}^{\text{eff}} \hat{P}(\kappa^*) |\Psi_{1}^{\text{OCOO}}\rangle = E_1 |\Psi_{1}^{\text{OCOO}}\rangle,$$ \hspace{1cm} (2)

with

$$\hat{H}^{\text{eff}} = \hat{H} + \Delta^{\text{shift}} |\Psi_{0}^{\text{CASSCF}}\rangle \langle \Psi_{0}^{\text{CASSCF}}|,$$ \hspace{1cm} (3)

where $\hat{H}$ is the full Hamiltonian of the system and $\hat{P}(\kappa^*)$ a projector over a restricted set of determinants following an active space structure in the fixed $\kappa^*$ MOs basis set. The effective active-space Hamiltonian $\hat{P}(\kappa^*) \hat{H} \hat{P}(\kappa^*)$ is complemented with a parametrized $\Delta^{\text{shift}}$ projection (in practice $\Delta^{\text{shift}}/t = 10^8$) so that any eigenfunction with non-negligible decomposition on $|\Psi_{0}^{\text{CASSCF}}\rangle$ gets penalized. As a result, solving Eq. (3) produces $|\Psi_{1}^{\text{OCOO}}\rangle$ which is an “effective” ground state of the associated energy-shifted active-space Hamiltonian $\hat{P}(\kappa^*) \hat{H}^{\text{eff}} \hat{P}(\kappa^*)$.

In the second step of the OCOO method, we act on the orbital rotation parameter $\kappa$ to optimize the MOs. For this, we define a cost function to be minimized

$$\text{CF}(\kappa) = E_1(\kappa) + \lambda |\langle \Psi_{0}^{\text{CASSCF}} | \Psi_{1}^{\text{OCOO}}(\kappa) \rangle|^2.$$ \hspace{1cm} (4)

The latter includes (i) the regular orbital-rotation dependent energy

$$E_1(\kappa) = \langle \Psi_{1}^{\text{OCOO}}(\kappa) | \hat{H} | \Psi_{1}^{\text{OCOO}}(\kappa) \rangle$$ \hspace{1cm} (5)

(from state-specific CASSCF method), and (ii) an overlap penalty term with amplitude $\lambda$ (in practice $\lambda/t = 10^8$). The role of this second contribution is to counterbalance the energy minimization with a measure of orthogonality between $|\Psi_{0}^{\text{CASSCF}}\rangle$ and $|\Psi_{1}^{\text{OCOO}}(\kappa)\rangle$.

A summarized flow-chart of the OCOO algorithm is given in Figure 2. The iterative procedure based on Eq. (3) and Eq. (4) starts with $\kappa = \kappa_0$. At convergence, a multi-reference state is generated in an optimized basis set $B_1$ characterized by $\kappa = \kappa_1$. Let us stress that both steps of the OCOO process call for the calculation of scalar products between multi-reference wavefunctions expressed in two different basis sets, namely $B_0$ and $B_1$ (as shown in Eq. (3) and Eq. (4)). Convergence is reached as soon as the variation in the cost function Eq. (4) is less than $10^{-7}$t between two successive iterations.

**Numerical results**

Keeping in mind the difficult selection of the active space, the present study is focused on the construction of state-dependent MOs basis sets that preserve the orthogonality between the multi-reference wavefunctions. Evidently, a two-electron in two-orbital model system is not flexible enough to investigate orbital relaxation. Practically, the OCOO method was implemented on a model system (four-electron three-site) ruled by a Hubbard Hamiltonian (see Figure 1) inspired by a CAS[2,2] on top of a single inactive orbital. Given a set of hopping $t$ and on-site repulsion $U$ energies, the on-site potential $\mu$ value was varied and the ground and excited states energies were calculated based on either state-averaged CAS[2,2]SCF calculations (\textit{i.e.} a single set of MOs to describe both states), or state-specific schemes (\textit{i.e.} two sets of optimized MOs, CASSCF and OCOO for the ground and excited states, respectively). Whatever the strategy, both wavefunctions were expanded on four Slater determinants written as $|1T_{2}\rangle$, $|1T_{23}\rangle$, $|1T_{23}\rangle$ and $|1T_{3}\rangle$ where the in-
index "i" (or "i") stand for the i-th α-MO (or β-MO). Charge transfer phenomenon being a motivation in the present study, symmetric and anti-symmetric model systems were considered by varying the values on-site potentials (see Figure 1).

All numerical implementations and calculations presented in this paper were carried out within the python package QuantNBody (see Ref. 14) recently developed by one of us (SY). This package was designed to facilitate the numerical implementation of second quantization algebra and the manipulation of many-body wavefunctions. We used this numerical toolkit to build/diagonalize the Hubbard Hamiltonians, implement orbital optimizations and evaluate the non-trivial overlap between multi-reference wavefunctions expressed in different MOs basis. Electronic structures result from the competition between one-electron and two-electron contributions. Therefore, we first derived the eigenvalues of the one-body part of the Hubbard Hamiltonians \( \hat{h} \) for both systems to evaluate the so-called spectral band. The eigen-values are readily derived and the spectral band \( \Delta \epsilon \) of the symmetric trimer reads

\[
\Delta \epsilon = \sqrt{\mu^2 + 8t^2}.
\] (6)

For the anti-symmetric trimer, this value becomes

\[
\Delta \epsilon = 2\sqrt{\mu^2 + 2t^2}
\] (7)

Based on these model systems, the relevance of the OCOO approach was examined and our results were compared to full-CI calculations in a strong correlation regime \( U/t = 10 \). All results are shown in Figures 3 and 4.

First, as shown in the bottom left panels of the Figures, the ground state energy is faithfully reproduced by the CASSCF and SA-CASSCF calculations in the whole range of \( \mu \) values. From the system size, the orbitals relaxations are sufficient to retrieve most of the full-CI wavefunction with \(|\langle \Psi_0^{\text{CASSCF}} | \Psi_0^{\text{FCI}} \rangle| \sim 0.99 \) for \( \mu \neq 0 \). In the limit \( \mu = 0 \), the spectral bands are minimized (see Eq. 6 and 7) and the CAS[2,2] picture might be questionable (projections \( \sim 0.91 \)).

Since the ground state energy does not suffer from the use of SA-CASSCF MOs, one would like to evaluate the robustness of a state-average method in the evaluation of vertical excitation energies noted \( \Delta E \). Strong deviations with respect to full-CI are observed, and \( \Delta E \) can be over-estimated by a factor up to 2.5 (in worst case scenario seen in Figures 3 and 4, middle panels). Such shortcomings of the SA-CASSCF approach are anticipated when \( \Delta \epsilon/U < 1 \) as confirmed in the top left-panel of Figures 3 and 4. Therefore, the SA-CASSCF excitation energy deteriorates for \( \mu/t \sim 5 \) (symmetric trimer) and \( -10 < \mu/t < 10 \) (anti-symmetric trimer), revealing the inaccuracy of the state-average strategy.

In contrast, excellent agreement between \( E_1^{\text{OCOO}} \) and \( E_1^{\text{FCI}} \) is reached for both model systems as soon as the excited state MOs are optimized following the OCOO method. The excitation energy is perfectly recovered as soon as each multi-reference state is individually generated in its optimized basis set. A similar conclusion was reached from a non-systematic procedure in donor-acceptor compounds. It was suggested that orbital relaxation should be explicitly taken into account.

To get a better view on the MOs modifications, the excited state wavefunction \(|\Psi_1^{\text{OCOO}}\rangle\) was expanded in the ground state basis set \( B_0 \). As shown in the right panel of Figures 3 and 4, the compact form constructed on the four configurations is lost, a feature of a deep change between \( B_0 \) and \( B_1 \) basis sets. Quantitatively, the projection of \(|\Psi_1^{\text{OCOO}}\rangle\) on the CAS[2,2] subspace defined in \( B_0 \) exhibits strong variations and can even become null. Besides, the zeroth-projection domain is reduced from \( \mu/t \in [0, 12] \) (Figures 3) to \( \mu/t \in [2, 3] \) (Figures 4) upon symmetry-breaking. These observations support the idea of the ill-definition of the \( B_0 \) basis set for the compact active-space representation of the first excited state in the strong correlation regime \( (U/t = 10) \) of symmetrical systems (e.g. mixed-valence compounds). Finally, note that all our conclusions and analysis remain unchanged in weaker correlation regimes \( (\text{i.e. } U/t = 5, \text{not shown here}) \) for which the domain calling for a simultaneous optimizations of the ground and excited states orbitals is reduced.
Figure 3: **Symmetric three-site Hubbard model with tunable on-site potential on the central site** (strong correlation regime: $U/t = 10$). Left panel: Energies obtained from FCI (in black), SA-CASSCF (in green) and with the combination CASSCF+OCOO (in orange), respectively for the ground and first excited states. The middle panel gives the vertical excitation energies obtained with the three methods. The upper panel shows the ratio $\Delta \epsilon / U$. Right panels: Decompositions of the multi-reference $|\Psi_{0}^{\text{CASSCF}}\rangle$ and $|\Psi_{0}^{\text{OCOO}}\rangle$ in the $B_{0}$ basis set. For the latter, strong variations are observed, stressing the deep basis set modifications.

Figure 4: **Anti-symmetric three-site Hubbard model with tunable on-site potential on left and right sites** (strong correlation regime: $U/t = 10$). Left panel: Energies obtained with FCI (in black), SA-CASSCF (in green) and with the combination CASSCF+OCOO (in orange) respectively for ground and first excited state. The middle panel gives the vertical excitation energies obtained with the three methods. The upper panel shows the evolution of the ratio $\Delta \epsilon / U$. Right panels: Decompositions of the multi-reference $|\Psi_{0}^{\text{CASSCF}}\rangle$ and $|\Psi_{1}^{\text{OCOO}}\rangle$ in the $B_{0}$ basis set. For the latter, strong variations are observed, stressing the deep basis set modifications.
Conclusion

An orthogonality constrained orbital optimization (OCOO) method is suggested and implemented to foresee the correlation regimes where orbitals relaxations cannot be ignored. The structure of the ground state is of CASSCF-type, whereas the excited state is defined as the lowest-lying orthogonal multi-reference one. Based on a trimer model system ruled by a Hubbard Hamiltonian, the excitation energy is evaluated from a multi-reference state-specific description of orthogonal states. As soon as the one-site energy $U$ competes with the spectral band $\Delta \epsilon$, SA-CASSCF calculations fail to reproduce the vertical excitation energy. Despite its simplicity, the model not only offers a practical method to democratically treat the ground and excited states, but also identifies correlation regimes where the robustness of SA-CASSCF might be questionable to reach spectroscopic accuracy. Finally, this work aims at re-emphasizing the importance of orbital optimization in zeroth-order multi-reference wavefunctions expansions. Explorations on the benefit of second-order perturbation treatment are planned to stress the decisive choice of MOs basis sets.

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