Automated construction of molecular active spaces from atomic valence orbitals

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We introduce the atomic valence active space (AVAS), a simple and well-defined automated technique for constructing active orbital spaces for use in multi-configuration and multi-reference (MR) electronic structure calculations. Concretely, the technique constructs active molecular orbitals capable of describing all relevant electronic configurations emerging from a targeted set of atomic valence orbitals (e.g., the metal $d$ orbitals in a complex). This is achieved via a linear transformation of the occupied and unoccupied orbital spaces from an easily obtainable single-reference wavefunction (such as from a Hartree-Fock or Kohn-Sham calculations) based on projectors to targeted atomic valence orbitals. We discuss the background, theory, and implementation of the idea, and several of its variations are tested. To demonstrate the performance and accuracy, we calculate the excitation energies for various transition metal complexes in typical application scenarios. The described technique makes MR calculations easier to execute, easier to reproduce by any user, and simplifies the determination of the appropriate size of the active space required for accurate results.
I. INTRODUCTION

Multiconfigurational and multireference (MR) methods remain indispensable in the treatment of challenging electronic structure problems. Transition metal complexes provide a rich source of examples, as they often feature strongly correlated electronic degrees of freedom, which render density functional theory (DFT) calculations unreliable. Unfortunately, MR methods require an a priori choice of a suitable set of active molecular orbitals (an active space), which critically determines the quality of the results. The choice of active space is non-trivial and often represents a major challenge in practical computations.

The standard way to choose an active space is as follows: First, a full set of molecular orbitals of the molecule is computed with a simple electronic structure method, such as Hartree-Fock (HF) or Kohn-Sham DFT (KS-DFT). Second, these molecular orbitals, both occupied and unoccupied, are visually inspected, and based on their shape, energy, occupation numbers, etc., one selects into the active space the set of orbitals which are expected to be chemically most relevant (e.g., with significant transition metal $d$-electron character or ligand character in the case of transition metal complexes—regions which are empirically known to be important). But despite the existence of general advice on how to select a good set of starting orbitals,$^1$–$^3$ there are some problems with this approach. First, the selection of molecular orbitals for the active space is performed by the user, normally based on personal experience and subjective criteria. This makes MR methods hard to apply, and gives results that are hard to reproduce and hard to judge in terms of quality. This stands in contrast to single-reference calculations which do not require active spaces and therefore do not have this level of arbitrariness. Second, the molecular orbitals mix together valence orbitals of different character; for example, typically a metal’s $d$ atomic valence orbitals contribute to a very large number of molecular orbitals, and it is often not easy to truncate these to a small active subset in such a way that they retain the capability of describing all the right physics in complicated systems. In the case of large complexes, especially with multiple metal ions, this procedure commonly becomes a matter of trial and error.

Techniques to aid in the construction of high quality active spaces are therefore highly desirable, particularly as more powerful electronic structure methods are becoming available which are capable of treating increasingly large active spaces efficiently.$^4$–$^2$ There have been a number of contributions in this area, and the general procedures can loosely be summarized as based on estimating the (correlated) occupation numbers of the orbitals (including the full single orbital
density matrix in Ref. 22), followed by selecting the active orbitals based on partial occupancy according to an input threshold. The various techniques differ primarily in how the occupation number information is obtained. For example, correlated occupation numbers can be estimated from unrestricted Hartree-Fock or Kohn-Sham calculations or from correlated calculations, such as MP2 or approximate DMRG calculations.

Nonetheless, while these existing automated approaches advance on the adhoc active space constructions, there is still room for further improvement. For example, an obvious drawback of the above procedures is that they all require a non-trivial preliminary calculation: either a correlated calculation must be performed, or a suitable broken symmetry solution must be found. This is not always possible: for example, there may not always be a broken symmetry solution involving the region of interest, or the preliminary correlated calculation may simply be too costly. A perhaps less obvious drawback, but one which one encounters in practice, is that there is no guarantee that the active orbitals found in these automated procedures are actually spatially located in the region of chemical interest. For example, in models of enzymatic binding sites, particularly those with charged ligands, the unpaired electrons may lie in functional groups which are spatially far from and irrelevant to the chemistry of the metal center. In this case, an additional inspection is once again required to choose the subset of active orbitals of chemical interest.

Here we propose an alternative approach to construct molecular active spaces for multireference problems automatically and systematically, which does not suffer from the drawbacks mentioned above, and which is particularly well-suited for practical calculations involving transition metal complexes. In its simplest formulation, the procedure requires only an easily obtained single-determinant reference function, together with a choice of target atomic valence orbitals. The technique is based on the following idea: It is empirically known that one can typically identify a small set of atomic valence orbitals which give rise to the strong correlation effects (for example, d atomic valence orbitals in transition metal complexes). We therefore aim to construct a set of active molecular orbitals by defining them in terms of these atomic valence orbitals. Concretely, using simple linear algebra, we can define mathematical rotations of the occupied and virtual molecular orbitals which maximizes their given atomic valence character (e.g. 3d character). After this rotation, the relevant molecular orbitals to include into the active space can be selected automatically.

Sec. II explains the motivation, background, theory, and implementation of the construction proposed here. Sec. IV then describes criteria for judging the quality of the constructed active
spaces, and discusses its application to a large number of prototypical MR calculations of metal complexes. Sec. V describes conclusions and possible implication for future work.

II. THEORY

A. What is an active space?

Many naturally occurring stable molecules have an electronic structure which is qualitatively well described by a single-determinant self-consistent field (SCF) wave function, such as used in Kohn-Sham Density Functional Theory (KS-DFT) or Hartree-Fock (HF). In this case, the entire space of molecular orbitals (MO) is strictly divided into fully occupied and fully unoccupied molecular (spin-) orbitals. However, there are important classes of chemical systems in which this picture breaks down and where a superposition of multiple $N$-electron determinants is required to describe the electronic structure even qualitatively. This phenomenon is sometimes called strong correlation; prototypical cases in which it occurs are (a) the process of homolytic bond breaking, and (b) various kinds of transition metal complexes—particularly when the complex is in an overall low-spin state generated by coupling of the metal to other metals or redox non-innocent ligands, as frequently encountered in catalysis and in bio-inorganic systems.

Both of these prototypical cases share the same root cause: The occurrence of valence atomic orbitals with energy levels similar to other valence orbitals, but with poor orbital overlap, giving rise to small energy splittings between bonding and anti-bonding linear combinations. In these cases quantum resonances between both bonding and anti-bonding orbitals must be explicitly considered to qualitatively describe the electronic structure—and single-determinant wave functions are incapable of doing so, because in these each MO either is occupied or is not, but not both. The core idea developed in this manuscript is that in these two most important cases, the emergence of strong correlation is tightly linked to specific valence atomic orbitals, which are easy to identify. In the case of transition metals, these are the compact $d$ orbitals (and possibly some specific ligand orbitals), and in the case of bond dissociation, these are the valence atomic orbitals of the dissociating atom(s). Thus, in the following we will assume that a small number of specific valence atomic orbitals are explicitly selected by the user (e.g., the $d$ orbitals of metal centers), and that the goal is to construct an active space suitable for describing all highly relevant determinants that they give rise to. We stress that this initial selection is easy in practice—the core problem is how
to use the information to build a suitable active space.

We thus briefly consider what an active space is. An active space wavefunction is one where the superpositions of determinants are restricted so that varied occupations are found only within the active orbitals \(\{\varphi_1 \ldots \varphi_m\}\). Technically, this means that the wavefunction can be written as a second quantized product

\[
|\Psi\rangle = \{\varphi_1 \ldots \varphi_m\}|\text{core}\rangle
\]

where \(\{\varphi_1 \ldots \varphi_m\}\) denotes a general occupancy wavefunction within the active orbitals, and \(|\text{core}\rangle\) denotes a single determinant. It is clear that the active orbitals must span the space of our chosen specific valence atomic orbitals. However, Eq. (1) additionally implies that the rest of the molecule must be well described by the single core determinant. To achieve this, the active space must contain orbitals additional to our set of specific valence atomic orbitals, and to remain compact, we need to define the minimal additional set.

To this end, we here employ the basic observation in density matrix embedding theory (DMET),\textsuperscript{29–36} which describes how to construct such an active space explicitly. In particular, DMET tells us that the active space with the above properties is at most twice the size of the initial set of chosen valence atomic orbitals. However, in this work we modify the presentation and practice of the DMET procedure to make it more natural in the active space setting. In particular, in contrast to the original presentation in references\textsuperscript{29,30} (but as described in the appendix of Ref. \textsuperscript{31}) we do not introduce separate “fragment” and “bath” orbitals, but rather retain the occupied and virtual character of the constructed active orbitals. This has the important benefit that it leads to a natural truncation procedure, which allows us to further reduce the size of the active space in the most chemically meaningful way. In Sec. II B we describe the isolation of entangled orbitals for the active space construction, and Sec. II C will provide technical details and discuss various practical aspects relevant in the active space case.

### B. Isolating target-overlapping orbitals for the active space

Let \(A = \{|p\rangle\}\) denote the (small) set of chosen target valence atomic orbitals (not necessarily orthonormal), which we expect to be responsible for strong correlations (e.g. the five 3\(d\) orbitals of a third row transition metal atom of a complex, details on their selection and representation will follow). Let \(|\Phi\rangle\) denote a Slater determinant, which represents the electronic structure of our system of interest at the SCF level (HF or KS-DFT).
Our method for active space construction is built around the following physical assumptions, which are those used in DMET\textsuperscript{29,30,32,37}:

(a) a SCF wave function $|\Phi\rangle$ may be unable to describe precisely how our target atomic orbitals are bonded with the rest of the molecule; however, it will generally describe the rest of the molecule reasonably (experience in DMET suggest that this works even in cases where the SCF wave function as a whole is qualitatively very wrong\textsuperscript{30}), and

(b) we can isolate the part of $|\Phi\rangle$ which involves our target AOs from the part which does not, and employ the former part as the active space (therefore allowing it to be replaced by a more powerful wave function description), and retain the simple determinantal description of rest.

To this end, we employ a rotation within the set of occupied molecular orbitals of $|\Phi\rangle$ which splits them into two groups: one group which has overlap with our target AOs, and one group which does not. A simple dimensional counting argument will show that for a set of $|A|$ selected target AOs, there is a rotation of the occupied molecular orbitals such that at most $|A|$ of them have non-zero weight on the target AOs. We similarly split the set of virtual molecular orbitals into one group of at most $|A|$ virtual orbitals which have weight on the target atomic valence orbitals, and the other group which does not. The idea is now to explicitly construct these rotated orbital groups, and then employ the at most $2|A|$ combined occupied and virtual orbitals with target overlap as active orbitals, while leaving the other occupied and virtual orbitals without target overlap as inactive (closed-shell) or virtual orbitals, respectively, in the following multi-configuration treatment. As all of the selected AOs in $A$ then lie within the span of this active space, the resulting multi-configurational wave function is then capable of representing arbitrary quantum resonances involving the target AOs.

We first discuss the occupied case. Let $i = 1 \ldots N_{\text{occ}}$ denote $N_{\text{occ}}$ occupied molecular orbitals (MOs) of $|\Phi\rangle$. The projector $\hat{P}$ onto the space of atomic orbitals in $A$, is given by

$$\hat{P} = \sum_{p,q\in A} |p\rangle [\sigma^{-1}]_{pq} \langle q|$$

(2)

Here $\sigma$ denotes the $|A| \times |A|$ target AO overlap matrix with elements $[\sigma]_{pq} = \langle p|q\rangle$, and $\sigma^{-1}$ its matrix inverse.

Employing these projectors, we construct the first set of active orbitals by rotating $|\Phi\rangle$’s occupied MOs $\{\langle i|\}$ as follows. First, we calculate the $N_{\text{occ}} \times N_{\text{occ}}$ overlap matrix of occupied orbitals projected onto span($A$), the space of selected target atomic orbitals:

$$[S^A]_{ij} = \langle i|\hat{P}|j\rangle$$

(3)
where $i, j$ are occupied orbital indices. Next we compute the $N_{\text{occ}} \times N_{\text{occ}}$ (unitary) matrix of eigenvectors $[U]_{ij}$ of $S^A$, such that

$$S^A U = U \text{diag}(\sigma_1, \ldots, \sigma_{N_{\text{occ}}}) \quad (4)$$

(where $\text{diag}(\ldots)$ denotes a diagonal matrix of the given elements), or, written in component form,

$$\forall i, j: \sum_k [S^A]_{ik}[U]_{kj} = [U]_{ij}\sigma_j. \quad (5)$$

There are at most $|A|$ non-zero eigenvalues $\{\sigma_i\}$, because $\text{span}(A)$ is a $|A|$-dimensional space, and $[S^A]_{ij}$ involves a projection onto it. Furthermore, the eigenvectors $[U]_{ij}$ of $S^A_{ij}$ define a rotation on the occupied orbitals:

$$|i\rangle \mapsto |\tilde{i}\rangle = \sum_k |k\rangle [U]_{ki}, \quad (6)$$

which clearly separates them into two groups: The at most $|A|$ rotated occupied orbitals $|\tilde{i}\rangle$ with $\sigma_i \neq 0$, which have non-vanishing overlap with our target atomic orbitals (and which therefore should go into the active space), and the remaining $|\tilde{i}\rangle$ with $\sigma_i = 0$ which have no overlap with our target atomic orbitals, and therefore can stay as inactive (inner closed shell) orbitals in the subsequent multiconfigurational methods.

Note that the rotated occupied orbitals $\{|\tilde{i}\rangle\}$ in (6) are obtained as a unitary transformation of $|\Phi\rangle$’s original occupied orbitals $\{|i\rangle\}$. Consequently, a determinantal wave function $|\Phi\rangle$ built from the $\{|\tilde{i}\rangle\}$ is physically equivalent (differs by at most a phase factor) from the original determinant $|\Phi\rangle$. That is, so far we have done nothing to $|\Phi\rangle$ except for splitting its occupied orbitals into a convenient set of at most $|A|$ orbitals related to our $|A|$ target AOs and the remaining set we can treat as inactive.

We then proceed similarly for the virtual orbitals $\{|a\rangle, 1 = 1 \ldots, N_{\text{vir}}\}$ of $|\Phi\rangle$: We form the $N_{\text{vir}} \times N_{\text{vir}}$ projected overlap matrix

$$[\tilde{S}^A]_{ab} = \langle a|\hat{P}|b\rangle, \quad (7)$$

where $a, b$ are virtual orbital indices, then find its unitary matrix of eigenvectors $\tilde{U}$ such that

$$\tilde{S}^A \tilde{U} = \tilde{U} \text{diag}(\sigma_1, \ldots, \sigma_{N_{\text{vir}}}) \quad \Leftrightarrow \quad \forall a, b: \sum_c [\tilde{S}^A]_{ac}[\tilde{U}]_{cb} = [\tilde{U}]_{ab}\sigma_c. \quad (8)$$

and use $\tilde{U}$ to rotate the virtual orbitals via

$$|a\rangle \mapsto |\tilde{a}\rangle = \sum_c |c\rangle [\tilde{U}]_{ca}. \quad (9)$$
Again, the at most $|A|$ of the new virtual orbitals $\{|\tilde{a}\rangle\}$ with eigenvalues $\sigma_a \neq 0$ are selected for the active space, while the remaining orbitals will stay unoccupied in the subsequent multi-configuration treatment.

Finally, having active orbitals with overlap with $A$ from both sides, occupied and unoccupied orbitals in $|\Phi\rangle$, we can form the total active space by combining the sets of $\{|\tilde{i}\rangle\}$ and $\{|\tilde{a}\rangle\}$ with non-zero projected overlap eigenvalues. Since the combined set includes all orbitals which have non-vanishing overlap with our target space span($A$), all of the selected AOs in $A$ then lie within the span of this active space. Therefore, a multi-configurational wave function with this active space will be capable of representing arbitrary quantum resonances involving the target AOs, which was the goal of our construction.

C. Technical details of the construction

Sec. II B discusses the formal framework of the active space construction. However, several practical aspects still need to be discussed: (a) How are the target AOs $A = \{|p\rangle\}$ chosen and represented? (b) How are the actual rotation matrices $U$ (eq. (6)) and $\bar{U}$ (eq. (9)) computed in practice? (c) Can the active space (formally twice the number of the target AOs) be further reduced in size? (d) How should open-shell systems be handled? (In particular, what to do for restricted open-shell functions $|\Phi\rangle$?) We will discuss these questions in the current and next subsections.

Let us first assume that $|\Phi\rangle$ is a closed-shell Slater determinant obtained from an SCF calculation. Its occupied and virtual molecular orbitals are expressed as:

\begin{align*}
|i\rangle &= \sum_{\mu \in B_1} |\mu\rangle C_i^\mu \\
|a\rangle &= \sum_{\mu \in B_1} |\mu\rangle \tilde{C}_a^\mu ,
\end{align*}

where $\mu$ are basis functions from the (large) computational basis set $B_1$ (e.g., cc-pVTZ or def2-TZVPP), and $C_i^\mu = [C_{\text{occ}}]_{\mu i}$ and $\tilde{C}_a^\mu = [C_{\text{vir}}]_{\mu a}$ are the coefficients of the basis function $\mu$ in the expansion of the occupied orbital $i$ and virtual orbital $a$ MOs, respectively. $C_{\text{occ}}$ and $C_{\text{vir}}$ denote the $|B_1| \times N_{\text{occ}}$ occupied and $|B_1| \times N_{\text{vir}}$ virtual sub-matrices of the $|B_1| \times |B_1|$ SCF orbital matrix $C$ (note that $N_{\text{occ}} + N_{\text{vir}} = |B_1|$—each orbital is either occupied or virtual).

In general, computational basis sets such as $B_1$ do not contain basis functions directly corresponding to AOs of any sort. For this reason, we here select our target AOs $A = \{|p\rangle\}$ based on a
second auxiliary basis set $B_2$. This is a minimal basis set of tabulated free-atom AOs (here MINAO is used\textsuperscript{38}, but other choices such as ANO-RCC subsets could be considered). This choice leads to simple expressions for the projected overlap matrices

$$S^A_{ij} = \langle i | \hat{P} | j \rangle = \sum_{\mu \mu'} C^\mu_i P_{\mu \mu'} C_{j}^{\mu'}$$

(11)

$$\tilde{S}^A_{ab} = \langle a | \hat{P} | b \rangle = \sum_{\mu \mu'} \tilde{C}^\mu_a P_{\mu \mu'} \tilde{C}_{b}^{\mu'} ,$$

(12)

where the matrix elements of the projector are

$$P_{\mu \mu'} = \sum_{pp'} \langle \mu | p \rangle \sigma^{-1}_{pp'} \langle p' | \mu' \rangle .$$

(13)

Combining all formulas into a numerical algorithm, the rotated orbitals are constructed as follows:

- Let $A \subset B_2$ denote the subset of AOs we choose as target AOs for the active space construction (for example, the five $3d$ AOs in a transition metal complex with one metal center).

- Form the overlap matrix $\sigma$ with elements $\sigma_{pp'} = \langle p | p' \rangle$, where $p, p' \in A$, and its inverse matrix with elements $\sigma^{-1}_{pp'}$. Both matrices have dimension of $|A| \times |A|$.

- Form the overlap matrix $S_{21}$ between the functions of $A \in B_2$ and the functions of the large basis set $B_1$, with elements $[S_{21}]_{\mu \mu} = \langle p | \mu \rangle$.

- Form the projector $P_{\mu \mu'} = \sum_{pp'} \langle \mu | p \rangle \sigma^{-1}_{pp'} \langle p' | \mu' \rangle$, or $P = S_{21}^\dagger \sigma^{-1} S_{21}$.

- Form the projected overlap matrices $S^A = C_{occ}^\dagger P C_{occ}$ for the occupied orbitals (eq. (11)), and $\tilde{S}^A = C_{vir}^\dagger P C_{vir}$ for the virtual orbitals (eq. (12)).

- Finally, diagonalize both projected overlap matrices to obtain the transformation matrices separating the MO sets by overlap with span($A$). Concretely, diagonalize $S^A$ to obtain the eigenvector matrix $U$, and use it to find the transformed occupied orbital matrix $\tilde{C}_{occ} = C_{occ} U$. Then diagonalize $\tilde{S}^A$ to obtain the eigenvector matrix $\tilde{U}$, and use it to find the transformed virtual orbital matrix $\tilde{C}_{vir} = C_{vir} \tilde{U}$. These are the expansion coefficients of $\{ | \tilde{i} \rangle \}$ (eq. (6)) and $\{ | \tilde{a} \rangle \}$ (eq. (9)), respectively.

Rather than using the minimal basis $B_2$ directly, one could consider choosing the target AOs from a set of polarized AOs which take the molecular environment into account, such as the
Intrinsic Atomic Orbitals (IAOs).\textsuperscript{38} If the IAOs are given as
\[ |\tilde{\beta}\rangle = \sum_\mu |\mu\rangle T_{\mu\beta}, \]  
(14)
where \( T_{\mu\beta} \) denotes the elements of the \( |B_1| \times |B_2| \) IAO transformation matrix.\textsuperscript{38} this can be incorporated by updating the projection matrix in \( S_{ij}^A \) and \( S_{ab}^A \) in eqs. (11) and (12) as
\[ P = ST(T^\dagger ST)^{-1}T^\dagger S. \]  
(15)
For simplicity, we do not follow this approach in this work, and choose the target AOs directly from the minimal basis \( B_2 \) as described above.

D. Truncating the active space

The eigenvalues \( \sigma_i \) and \( \sigma_a \) of the projected overlap matrices in eqs. (6) and (9) reflect the degree to which the transformed orbitals \( |i\rangle \) and \( |a\rangle \) overlap with the space of our target AOs. If we include every such transformed orbital with \( \sigma_a \neq 0 \) and \( \sigma_i \neq 0 \) into our active space, the resulting CAS space will exactly include all electronic configurations which can be formed over the given AOs and the maximum size of the CAS space is twice that of the target AO space. However, this CAS space may be too large and we may need to truncate it. Here we can use the fact that often many of the \( \sigma_i \) and \( \sigma_a \) are small. As a practical measure, we can set a threshold, such as 0.05–0.1, to exclude MOs with negligible overlap with span(A). In addition to reducing the size of the active space, this can further improve the reproducibility of calculations in the case of very small eigenvalues. This threshold becomes the only numerical parameter to be chosen by the user.

Of course, if truncation is used, the active space no longer captures all possible configurations which can be formed involving the target AOs. However, the truncation does \textit{not} affect the quality of the description of the rest of the molecule by the core determinant in Eq. (1). This guarantees that the CASCI energy lies below the variational HF energy. We can also imagine the opposite tradeoff, where one obtains a truncated active space which retains the ability to capture all possible configurations involving the target AOs, at the cost of worsening the quality of the core determinant which describes the rest of the molecule. (In DMET language, this would correspond to truncating the “bath” orbitals, which is considered in Refs.\textsuperscript{32} and\textsuperscript{37}). However, this may be a worse truncation procedure in the current setting, as the energy gained by treating the fluctuations in occupation number in the target AOs (such as a TM 3\textit{d} shell) may not make up for the energy
lost in incompletely describing the mean-field hybridization between the target AOs and the rest of the molecule. In particular, this second bath truncation procedure can, in principle, lead to a CASCI energy above the variational HF energy.

E. Treatment of open-shell systems

If \( |\Phi\rangle \) is a closed-shell determinant, then the active construction algorithm can be directly used as described in Sec. II C. However, in the case of open shell determinants, several choices can be considered:

1. One may perform the algorithm separately for alpha and beta orbitals, thus creating active orbitals with different spatial parts for alpha and beta-spin electrons. While this choice is the most straight-forward and, arguably, creates the best initial active orbitals in the open-shell case, this option is not directly feasible if a spin-adapted multiconfigurational calculation will follow—most existing MCSCF programs cannot use such unrestricted orbitals (although this is implemented in the code we use here\(^{39}\)). A possible remedy for this problem would be to construct a single set of “corresponding orbitals”\(^{40}\) from the separate alpha- and beta-orbital sets, but this has not been tested here.

2. One may use exclusively the alpha orbitals to construct the active space orbitals (and inactive orbitals determining the core determinant). This treatment can be applied to both restricted and unrestricted SCF functions \( |\Phi\rangle \) in a simple manner. The rationale for this is that in the restricted open-shell case, the occupied beta orbitals lie entirely within the linear span of the occupied alpha orbitals, so one can argue that this choice takes care of both spin cases. However, this argument is somewhat misleading because it may lead to some unoccupied beta orbitals to be transformed into the core space, therefore enforcing their occupation with two electrons. This error in the core means that the CASCI energy may be higher than the variational HF energy. If the singly-occupied MOs in \( |\Phi\rangle \) have only small components on the target valence AOs, this can lead to very bad CASCI wavefunctions.

3. If a ROHF determinant \( |\Phi\rangle \) is used, one may apply the construction of Sec. II C exclusively to the doubly-occupied and fully unoccupied orbitals of \( |\Phi\rangle \), to form the core determinant and initial part of the active space, and then include additionally all the singly-occupied orbitals of \( |\Phi\rangle \) into the active space. The CASCI energy is then guaranteed to be below the
variational HF energy, and further spin-adaptation can be used. The main drawback is that the active space is usually larger in this procedure.

By default, we use method 2, however, we compare the different schemes in one of the systems below.

III. COMPUTATIONAL DETAILS

We implemented the atomic valence active space (AVAS) construction within the PySCF\textsuperscript{39} package. All Complete Active Space Self-Consistent Field (CASSCF), Complete Active Space Configuration Interaction (CASCI), and strongly contracted $N$-electron valence state perturbation theory (NEVPT2)\textsuperscript{41–44} calculations were carried out using PySCF. For active spaces with more than 16–17 orbitals we used the BLOCK code\textsuperscript{45} through the PySCF-BLOCK interface to perform DMRG calculations in the active space.

For simplicity, we used all-electron cc-pVTZ-DK\textsuperscript{46,47} basis sets for all the systems. For the auxiliary minimal basis $B_2$ used to choose the target AOs, we employed the MINAO basis\textsuperscript{38}, which is a truncated subset of the cc-pVTZ basis; for most atoms, this set consists of spherically averaged ground-state Hartree-Fock orbitals for the free atoms. We did not use point group symmetry in the present calculations, since in a straight-forward implementation, the MOs do not necessarily retain symmetry-adaption after rotation; however, if symmetry-adaptable sets of target AOs are chosen, symmetry respecting orbital rotations can in principle be constructed. For completeness, scalar relativistic effects were included using the exact-two-component (X2C) approach\textsuperscript{48,49}, but this did not lead to significant differences from the non-relativistic calculations in any of the considered examples. Spin-orbit coupling was not considered.

IV. RESULTS AND DISCUSSION

Judging the quality of an active space is not trivial. Here we employ two complementary criteria:

1. In the course of a CASSCF calculation, the active space orbitals are optimized. If the overlap of the optimized active space with our initial active space guess remains high, our active space guess is of high quality. To quantify this aspect, we compute the $N_{\text{act}} \times N_{\text{act}}$ overlap
between the initial guess and optimized final active orbitals, and compute its singular value decomposition. If all singular values are close to 1.0, the active space remains mostly unchanged. On the contrary, each singular value close to 0.0 indicates that an initial active orbital has been completely replaced by an unrelated orbital, indicating a bad initial guess.

2. We compare our computed excitation energies to experimental results and other high-level calculations reported in the literature. When constructing a well-behaved series of active spaces, we should be able to see convergence or stability of the computed properties with respect to the active space size.

We now apply these criteria in calculations on transition-metal complexes.

A. Ferrocene

We begin by considering the electronic structure of ferrocene, Fe(C₅H₅)₂. The ground state of ferrocene is dominated by a single configuration with Fe d⁶. MO analysis in Ref. 50 and our CI expansion coefficients indicate that the lowest excited states of ferrocene have significant multiconfigurational character.

We carried out an initial restricted Hartree-Fock (ROHF) calculation for the singlet ground state. We used the optimized D₅ᵥ geometry from Ref. 51 (using the cc-pw-CVTZ basis set at the CCSD(T) level). In this geometry, the two cyclopentadienyl (Cp) rings are planar and the z-axis is aligned with the Cp-Fe-Cp axis.

As our target set of AOs, we first chose the five 3d orbitals of Fe. Using a threshold of 0.1, the AVAS scheme produces a seven orbital active space: five orbitals from the occupied orbital space and two orbitals from the unoccupied orbital space. The five overlap eigenvalues above the threshold from the occupied space are 0.325, 0.325, 0.973, 0.973, 0.995, and the two eigenvalues from the unoccupied space are 0.675, 0.675. There are three omitted unoccupied orbitals: two of them have only 2.7% weight in the 3d AO space and (3dₓᵧ, 3dₓ²−ᵧ²) character, and one has 0.6% weight in the 3d AO space, corresponding to the 3d𝑧² AO. The two orbitals from the occupied orbital space with eigenvalues 0.325 and 0.325, as well as the two selected MOs from the unoccupied orbital space with eigenvalues 0.675, 0.675, both have (3dₓz, 3dᵧz) character; based on
this, we conclude that \((3d_{xz}, 3d_{yz})\) are most strongly involved in bonding with the two Cp rings, in agreement with the bonding picture established in earlier studies\(^{50,52}\).

To construct a second, larger active space, we next included the ten \(p_z\) orbitals of the carbon atoms in the Cp rings into the target AO list. The AVAS construction then yields 15 orbitals above the 0.1 overlap threshold, giving an (18e,15o) active space: 9 of occupied character and 6 of unoccupied character. Lowering the threshold to 0.05 gives a (22e,17o) active space.

We calculated the ground state and singlet and triplet excited states of ferrocene with these active spaces at the CASCI and CASSCF level. Previous studies\(^{50}\) indicate that there are three low-lying \(d \rightarrow d\) singlet transitions \((1^1E''_2, 1^1E''_1, 2^1E''_1)\) and three low-lying \(d \rightarrow d\) triplet transitions \((1^3E''_2, 1^3E''_1, 2^3E''_1)\). These \(d \rightarrow d\) transitions describe excitations from the three non-bonding orbitals (predominantly of \(3d_{x^2-y^2}, 3d_{xy}\) and \(3d_z^2\) metal character, as described above) to the two antibonding orbitals having mostly \((3d_{xz}, 3d_{yz})\) metal character. All these excited states have multi-configurational (but single-excitation) character. Note that the \(E''_1\) and \(E''_2\) states are doubly degenerate, thus there are 6 low-lying singlet and triplet excited states. In the CASSCF calculations we therefore state-averaged over 7 roots and 6 roots in the singlet and triplet manifolds respectively.

Table I displays the excitation energies, compared to experimental and theoretical numbers from the literature, including singly excited configuration interaction (SECI)\(^{53}\), symmetry adapted cluster configuration interaction (SAC-CI)\(^{50}\) and time-dependent density functional theory (TD-DFT) calculations\(^{54}\). Table III compares the impact of using different active spaces with different methods.

The performance of CASCI for the smallest (10e,7o) active space is reasonable for most of the excited states except for the \(2^1E''_1\) and \(2^3E''_1\) states. These two states have some Rydberg character\(^{50}\) thus the valence CASCI overestimates these transitions by about 2 eV, as can also be seen in the errors of the SECI energies. (Including the truncated orbitals with eigenvalues less than 0.1 into the active space changed the excitation energies by less than 0.01 eV). Averaging over all the states in the CASSCF seemed to spread the error over the states, lowering all the energies. An accurate description of the differential correlation in the \(2^1E''_1\) and \(2^3E''_1\) states thus requires a dynamic correlation treatment. We find excellent agreement for all states at the CASSCF+NEVPT2 level, with a largest error of only 0.21 eV.

The larger active spaces including the ligand \(\pi\) orbitals do not improve the CASSCF excitation energies except for the \(2^1E''_1\) and \(2^3E''_1\) states. However, incorporating dynamic correlation through NEVPT2 rebalances the states, with good agreement with experiment and the CASSCF+NEVPT2
excitation energies from the smaller active space. Together, these observations indicate that the multiconfigurational character is already well converged in the smaller active space.

As discussed above, a second test of the quality of the AVAS active space is provided by the SVD decomposition of the overlap between the CASSCF-optimized active space and the initial guess. In the case of ideal coincidence the SVD eigenvalues should be equal to 1. The smallest SVD eigenvalue was 0.927 for the (10e,7o) active space and 0.906 for the (18e,15o) active space, respectively. This indicates that the AVAS provides a stable and accurate initial guess for the CASSCF procedure.

**TABLE I: The lowest singlet and triplet excitation energies of ferrocene, calculated with the (10e,7o) active space. All energies are in eV.**

<table>
<thead>
<tr>
<th>State</th>
<th>CASCI(\text{10e,7o})</th>
<th>CASSCF(\text{10e,7o})</th>
<th>CASSCF+NEVPT2(\text{10e,7o})</th>
<th>SAC-CI\textsuperscript{50}</th>
<th>SEC\textsuperscript{53}</th>
<th>TD-DFT\textsuperscript{54,55}</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1^1E'')</td>
<td>2.85</td>
<td>2.10</td>
<td>2.79</td>
<td>2.11</td>
<td>2.63</td>
<td>2.90</td>
<td>2.8\textsuperscript{55}, 2.7\textsuperscript{56}</td>
</tr>
<tr>
<td>(1^1E'')</td>
<td>3.33</td>
<td>2.17</td>
<td>2.87</td>
<td>2.27</td>
<td>3.31</td>
<td>3.03</td>
<td>2.81\textsuperscript{55}, 2.98\textsuperscript{56}</td>
</tr>
<tr>
<td>(2^1E'')</td>
<td>5.82</td>
<td>4.07</td>
<td>3.99</td>
<td>4.03</td>
<td>5.74</td>
<td>3.60</td>
<td>3.82\textsuperscript{55,56}</td>
</tr>
<tr>
<td>(1^3E_1)</td>
<td>1.81</td>
<td>0.97</td>
<td>1.88</td>
<td>1.40</td>
<td>1.81-1.87</td>
<td>1.74\textsuperscript{55}</td>
<td></td>
</tr>
<tr>
<td>(1^3E_2)</td>
<td>1.84</td>
<td>1.07</td>
<td>2.03</td>
<td>1.68</td>
<td>1.81-1.87</td>
<td>2.0\textsuperscript{55}</td>
<td></td>
</tr>
<tr>
<td>(2^3E_1)</td>
<td>4.26</td>
<td>2.25</td>
<td>2.50</td>
<td>2.60</td>
<td>4.56</td>
<td>2.29-2.34\textsuperscript{55}</td>
<td></td>
</tr>
</tbody>
</table>

**B. [Fe(NO)(CO)\textsubscript{3}]^-**

We next consider the complex anion [Fe(NO)(CO)\textsubscript{3}]\textsuperscript{-}, which exhibits catalytic activity in a range of organic reactions, and has been extensively characterized both theoretically and experimentally (see Ref.\textsuperscript{57} and references therein). The complex features three-center bonds along both the Fe–N–O axis and between Fe and each pair of CO ligands\textsuperscript{57} its catalytic mode of action exhibits a highly unusual nitrosyl-ligand based oxidation in some cases,\textsuperscript{58} and response to photo-activation in other cases\textsuperscript{59} Analysis of the ground-state CASSCF wavefunction and natural orbital occupations indicates that it has some multiconfigurational character, and that it should be thought
TABLE II: The lowest singlet and triplet excitation energies of ferrocene, calculated with various active spaces. All energies are in eV.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>CASCI (10e,7o)</th>
<th>CASCI+NEVPT2 (10e,7o)</th>
<th>CASSCF (10e,7o)</th>
<th>CASSCF+NEVPT2 (10e,7o)</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^1E''_2$</td>
<td>2.85</td>
<td>3.51</td>
<td>3.10</td>
<td>3.20</td>
<td>2.10</td>
</tr>
<tr>
<td>$1^1E'_1$</td>
<td>3.33</td>
<td>3.90</td>
<td>3.20</td>
<td>3.21</td>
<td>2.17</td>
</tr>
<tr>
<td>$2^1E''_1$</td>
<td>5.82</td>
<td>5.81</td>
<td>4.24</td>
<td>4.00</td>
<td>4.07</td>
</tr>
<tr>
<td>$1^3E''_1$</td>
<td>1.81</td>
<td>2.46</td>
<td>2.14</td>
<td>2.25</td>
<td>0.97</td>
</tr>
<tr>
<td>$1^3E''_2$</td>
<td>1.84</td>
<td>2.48</td>
<td>2.25</td>
<td>2.34</td>
<td>1.07</td>
</tr>
<tr>
<td>$2^3E''_1$</td>
<td>4.26</td>
<td>4.33</td>
<td>2.78</td>
<td>2.54</td>
<td>2.24</td>
</tr>
</tbody>
</table>

As in the previous example, we started with a RHF calculation for the singlet ground state and for the simplest active space we chose five 3d orbitals of Fe as the target AOs. We used the geometry of Ref. \cite{59}. Using an overlap threshold of 0.1 gives rise to five occupied orbitals and three unoccupied orbitals for the active space; two unoccupied orbitals with only 6% weight in the 3d orbital space lie below the threshold for active space inclusion. Of the three unoccupied orbitals included in the active space, two have $(3d_{yz}, 3d_{xy})$ and $(3d_{xz}, 3d_{x^2-y^2})$ character, respectively, while the third one has mostly $3d_{z^2}$ character. Additionally including the nitrogen 2p orbitals with the same threshold in the set of target AOs gives a (16e,14o) space, adding three MOs with 2p character involved in the three-center Fe–N–O bonds, and three involved in N–Fe–CO type bonds.

Unfortunately, there is no gas phase experimental excitation data for this system. However, theoretical vertical excitation energies from state-averaged CASSCF calculations followed by MRCI+Q, using the def2-TZVPP basis set (omitting g-functions) have previously been reported\cite{59}, which we can compare against. We used CASSCF and NEVPT2 to compute the vertical transition energies averaging over five singlet and four triplet states, as in Ref. \cite{59}. The smallest SVD eigenvalue for the active space overlap with the initial guess for the (10e,8o) active space is 0.806, indicating that AVAS provides a good initial guess. For the (16e,14o) active space, the lowest
SVD eigenvalue decreases to 0.652—apparently adding only the nitrogen $2p$ orbitals, without also adding the carbon $2p$ orbitals, leads to a less balanced active space compared to the $(10e,8o)$ AVAS initial active space.

The vertical excitation energies from CASSCF with the $(10e,8o)$ active space are in better agreement with the CASSCF/MRCI+Q excitation energies than with CASSCF results from Ref. 59. This indicates that the $(10e,8o)$ active space constructed using AVAS provides a more balanced description of electron correlation than the larger active spaces.

However, the NEVPT2 dynamical correlation treatment significantly raises the obtained excitation energies above the MRCI+Q values. Similarly, CASSCF calculations with the larger $(16e,14o)$ active space also yield significantly higher excitation energies than with the $(10e,8o)$ active space, and the CASSCF+NEVPT2 excitation energies in this larger space are also fairly different from the values obtained from the $(10e,8o)$ active space. This lack of stability with respect to the active space size indicates that the excited states are not benign electronically, and that their accurate description requires a more sophisticated dynamic correlation treatment beyond 2nd order perturbation theory. This is supported by the MRCI+Q study in Ref. 59, where the (empirical) Q-contribution to the excitation energy is as large as 0.2 eV.

To further substantiate these claims, we also computed CASSCF+NEVPT2 results for the same manually selected $(14e,9o)$ initial active space as described in Ref. 59 (in these calculations, the initial 14 active orbitals were manually selected for Fe $d$ and NO $\pi$ and $\pi^*$-character by visual inspection of KS-DFT/PBE orbitals computed with the def2-TZVPP basis set; the CASSCF excitation energies thus obtained reproduced the results reported in the supporting information of Ref. 59 with better than 0.01 eV accuracy). By comparing the results of (our) NEVPT2 and (the referenced) MRCI+Q for the same active space of Ref. 59, we can separate the effect of the dynamic correlation treatment from the quality of the active space. We see that CASSCF+NEVPT2 calculations performed with our automatically constructed $(10e,8o)$ active space and the manually selected $(14e,9o)$ active space show a fair agreement in the case of singlet excited states; however, the CASSCF+NEVPT2 method overestimates the energies of the triplet excited states with the $(14e,9o)$ active space by 0.5–0.75 eV more than with the $(10e,8o)$ active space, compared to the CASSCF/MRCI+Q transition energies. Combined, these facts strongly suggest that the approximate NEVPT2 correlation treatment is the primary cause of deviation from the MRCI+Q reference values, rather our automatically constructed active space, and that the smaller AVAS provides a more balanced description of this system.
TABLE III: Vertical excitation energies from the ground state to the lowest singlet and triplet states of \([\text{Fe(NO)(CO)}_3]^-\). All energies are in eV.

<table>
<thead>
<tr>
<th>State</th>
<th>CASSCF (10e,8o) (16e,14o)</th>
<th>CASSCF+NEVPT2 (10e,8o) (16e,14o)</th>
<th>CASSCF$^{59}$ (14e,9o)*</th>
<th>CASSCF/MRCI+Q$^{59}$ (14e,9o)*</th>
<th>CASSCF+NEVPT2 (14e,9o)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_2$</td>
<td>3.14 4.37</td>
<td>4.04 3.76</td>
<td>2.78</td>
<td>3.26</td>
<td>4.13</td>
</tr>
<tr>
<td>$^1E$</td>
<td>3.58 4.86</td>
<td>4.29 3.98</td>
<td>3.18</td>
<td>3.53</td>
<td>4.29</td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>3.54 5.17</td>
<td>4.33 4.25</td>
<td>3.22</td>
<td>3.64</td>
<td>4.40</td>
</tr>
<tr>
<td>$^3A_1$</td>
<td>2.27 2.44</td>
<td>2.63 2.43</td>
<td>1.76</td>
<td>2.32</td>
<td>3.40</td>
</tr>
<tr>
<td>$^3E$</td>
<td>2.82 3.41</td>
<td>3.51 3.20</td>
<td>2.44</td>
<td>2.96</td>
<td>4.02</td>
</tr>
<tr>
<td>$^3A_2$</td>
<td>2.89 4.04</td>
<td>3.80 3.82</td>
<td>2.56</td>
<td>3.15</td>
<td>4.39</td>
</tr>
</tbody>
</table>

* The (14e,9o) active space consisted of all Fe $d$ orbitals and the NO $\pi$ and $\pi^*$

C. FeO$_4^{2-}$

As our next system, we consider the bare tetraoxoferrate (VI) ion, FeO$_4^{2-}$. We assume a tetrahedral FeO$_4^{2-}$ cluster with an Fe–O distance of 1.660Å.

We started with a ROHF calculation for the $^3A_2$ ground state. Including only 3$d$ orbitals into the target AO set gives a (8e,8o) active space. Three unoccupied MOs have 34.5% weight in the 3$d$ orbital space with 3$d_{yz}$, 3$d_{xz}$ and 3$d_{x^2-y^2}$ character, but are mostly centred on the ligands, while the occupied MOs have mostly metal character. This indicates that some of the low-lying excitations are charge-transfer excitations.

An earlier study$^{60}$ found that the ground and excited states cannot be described by a simple Ligand Field Theory $d^2$ model and contain superpositions of a large number of configurations, including ligand-to-metal excitations; from this it has been argued that it is insufficient to only consider molecular orbitals with Fe 3$d$ character in the active space to describe excited states. Indeed, we find CASSCF+NEVPT2 calculations with the (8e,8o) active space (generated only with the 3$d$ orbitals in the target AO set) significantly overestimate the excited states, by about $\approx 6500$ cm$^{-1}$, compared to experiment.

For this reason, we expanded the target AO list to the five 3$d$ orbitals of Fe and 2$p$ orbitals of all four O atoms. Using option2 to transform the alpha orbitals, our scheme with the 0.1 overlap threshold produced 14 occupied orbitals and 3 unoccupied orbitals, resulting in a (26e,17o) active
TABLE IV: Calculated and experimental low-lying excitation energies of FeO$_2^{2-}$. All energies are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>State</th>
<th>CASCI (26e,17o)</th>
<th>CASSCF (26e,17o)</th>
<th>CASCI+NEVPT2 (26e,17o)</th>
<th>CASSCF+NEVPT2 (26e,17o)</th>
<th>RASSCF$^{60}$ (26,4,0;12,5,0)</th>
<th>Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1E$</td>
<td>9882, 9899</td>
<td>7462</td>
<td>6252, 6268</td>
<td>6548, 6550</td>
<td>6300</td>
<td>6209, 6219$^{61}$</td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>14703</td>
<td>10710</td>
<td>9006</td>
<td>9471</td>
<td>9200</td>
<td>9119$^{61}$, 9176$^{62}$</td>
</tr>
</tbody>
</table>

We calculated the vertical excitation energies of FeO$_2^{2-}$, namely transition energies from the ground $^3A_2$ state to the first two excited states, $^1E$ and $^1A_1$ (see Table IV), using CASCI and CASSCF (state-averaged over three singlet states and one triplet state) and CASCI+NEVPT2, comparing to previously reported RASSCF and experimental numbers. The CASCI calculations significantly overestimate the excitation energies, however, this is significantly improved by optimizing the orbitals using state-averaged CASSCF. The smallest SVD singular value for the active space overlap between the initial and optimized active orbitals is 0.968, indicating that our initial active orbitals provide a very good guess for the CASSCF procedure and only require a little relaxation to yield good agreement with experiment.

Including dynamic correlation by means of NEVPT2 on top of CASCI or CASSCF significantly improves the results. Note that the difference between our CASSCF excitation energies and those in Ref. 60 with 17 orbs, obtained with the RASSCF method reflects both the slightly different basis as well as truncated CI space in RAS.

D. VOCl$_2^{2-}$

We now consider the oxotetrachlorovanadate(IV) anion, VOCl$_2^{2-}$. We use a square pyramidal geometry for VOCl$_2^{2-}$ as in Ref. 63 (although we use a different orientation: the V atom is at the origin, the O atom is on the z axis above the x-y plane and the Cl atoms are below the x-y plane).

In this complex, vanadium is in a $d^1$ configuration. As in the next example, here the $d \rightarrow d$
excitations do not have much multiconfigurational character. However, it is important that multireference methods (and their active spaces) provide a balanced description of all states, not just multiconfigurational ones. The vanadium complex provides a system to test this in an early transition metal (single-reference) problem.

If we choose a set of five AOs, representing the five 3d orbitals of a vanadium atom, we obtain five occupied and four unoccupied MOs from the ROHF reference wavefunction using the AO-projector option 2. One of the occupied MOs is a non-bonding 3d$_{xy}$ atomic orbital, while the other V 3d orbitals atom strongly mix with the valence orbitals of the oxygen atom and four chlorine atoms. This results in four doubly occupied bonding MOs and four anti-bonding MOs which are unoccupied in the ground state. The two unoccupied MOs have 69.4% overlap with the 3d orbital space and carry (3d$_{xz}$, 3d$_{yz}$) character, other two have 54.0% and 70.3% overlap with the 3d orbital space and have (3d$_{z^2}$ and 3d$_{x^2−y^2}$) character, respectively; all four unoccupied MOs have mostly metal character.

Using the (9e,9o) active space we calculated the lowest transitions, which are essentially $d \rightarrow d$ in nature. There are four possible ligand-field transitions from the highest non-bonding 3d$_{xy}$ orbital to four unoccupied MOs, thus in CASSCF we averaged over five doublet states. Table VI summarizes the low-energy vertical $d \rightarrow d$ energies. The CASSCF method with the small (9e,9o) active space gives an accurate $^2B_1$ state, but strongly overestimates the other excited states. Using NEVPT2 to treat the dynamic correlation on top of CASSCF significantly improves the excited states, resulting in a good agreement with the experimental values and CASPT2 results obtained with the (11e,10o) space. The (11e,11o) space is similar to ours with the addition of the oxygen 2p shell.

We also construct a larger (33e,21o) active space, including the 2p orbitals of O and the 3p orbitals of Cl into the target AO list. In this larger space, to reduce computational cost, we used CASCI+NEVPT2 rather than CASSCF+NEVPT2. The excited states from CASCI+NEVPT2 with the (33e,21o) active space are also in excellent agreement with the experimental data. The stability of the CASCI/CASSCF+NEVPT2 excitations with respect to expanding the active space provides confirmation that the correlation is well converged by all these treatments.

The smallest SVD eigenvalue for the active space overlap with the initial guess in the CASSCF calculation with the (9e,9o) active space is equal to 0.821. This implies that in this case AVAS provides a reasonable, but not perfect guess for CASSCF.

We also used this complex to test and compare options 2 and 3 as described in Sec. II E for
TABLE V: Vertical excitation energies to the lowest excited doublet states from the ground $^2B_2$ state for VOCl$_4^{2-}$. All energies are in cm$^{-1}$.

<table>
<thead>
<tr>
<th>State</th>
<th>CASSCF (9e,9o)</th>
<th>CASSCF+NEVPT2 (9e,9o)</th>
<th>CASCI+NEVPT2 (33e,21o)</th>
<th>CASPT2$^{63}$ (11e,10o)</th>
<th>Exp.$^{64}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2B_1$</td>
<td>11736</td>
<td>13044</td>
<td>12123</td>
<td>12667</td>
<td>11600</td>
</tr>
<tr>
<td>$^2E$</td>
<td>18650</td>
<td>14537</td>
<td>13722</td>
<td>13620</td>
<td>13700</td>
</tr>
<tr>
<td>$^2A_1$</td>
<td>33808</td>
<td>28586</td>
<td>26824</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

constructing the active space with a ROHF reference determinant $|\Phi\rangle$. The excitation energies, calculated with these two options, differ by less than 100 cm$^{-1}$ ($\approx$0.01 eV). However, VOCl$_4^{2-}$’s ground state has only one singly occupied orbital, and it is possible that larger differences will occur for systems with ground states of higher spin.

E. [CuCl$_4$]$^{2-}$

We finally consider the $D_{4h}$ [CuCl$_4$]$^{2-}$ complex, with a Cu–Cl bond length of 2.291 Å, as in Ref. 63. As in the vanadium system, the $d \rightarrow d$ transitions are single-reference in character: this complex provides a late transition metal example.

Using the 3$d$ AOs of Cu as the target AOs and a default cutoff of 0.1, we obtain only 5 occupied MOs and no unoccupied MOs, which might be surprising at first glance. However, this is because the antibonding orbitals have ligand character, and thus there are no unoccupied MOs having more than 5% 3$d$ character. The lowest ligand-field transitions arise from the excitation of electrons from the doubly-occupied MOs with dominant 3$d$ character to the singly occupied MOs with 3$d$ character.

Despite the fact that the lowest transitions happen mostly within the 3$d$ orbital space, such a small (9e, 5o) active space is insufficient to describe them as the nearly filled space leaves no room for electron correlation. CASSCF+NEVPT2 however, provides good agreement with the experimental numbers (see Table VI). To see the effect of a larger active space, we also included the 3$p$ AOs of Cl in the target AO list, obtaining a (33e,17o) active space. The corresponding CASSCF
Table VI: The electronic states of [CuCl₄]²⁻. All energies are in cm⁻¹.

<table>
<thead>
<tr>
<th>State</th>
<th>CASSCF (9e,5o)</th>
<th>CASSCF+NEVPT2 (9e,5o)</th>
<th>CASSCF+NEVPT2 (33e,17o)</th>
<th>CASPT2 (11e,11o)</th>
<th>Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹²B₂g</td>
<td>6588</td>
<td>10675</td>
<td>10666</td>
<td>11321</td>
<td>10500⁵⁵</td>
</tr>
<tr>
<td>¹²E₉</td>
<td>8727</td>
<td>12832</td>
<td>12947</td>
<td>13379</td>
<td>12800⁵⁵</td>
</tr>
<tr>
<td>¹²A₁₉</td>
<td>9690</td>
<td>14021</td>
<td>14135</td>
<td>14597</td>
<td></td>
</tr>
</tbody>
</table>

Excitation energies are still poor, indicating that the necessary correlation is not of valence character. The CASSCF+NEVPT2 excitation energies in this larger space, however, remain in very good agreement with experiment. The insensitivity to active space indicates that correlations are well converged in the CASSCF+NEVPT2 treatment.

The smallest SVD eigenvalue for the active space overlap with the initial guess in converged CASSCF calculations is equal to 0.930 in the case of the small (9e,5o) active space and 0.985 for the (33e,17o) active space, indicating that AVAS provides a good initial guess for CASSCF.

V. CONCLUSIONS

In this work, we investigated how to systematically and automatically construct molecular active spaces solely from a single determinant wavefunction together with a list of atomic valence orbitals. The atomic valence active space (AVAS) procedure is based on a straightforward linear algebraic rotation of the occupied and unoccupied molecular orbital spaces which maximizes their given atomic valence character. The method automatically detects the valence bonding partners of a given atomic valence orbital, and, by using a single small threshold, can also detect non-bonding orbitals without constructing spurious partners (either occupied or unoccupied).

To test our scheme, we tested both the quality of our orbitals as initial guesses for CASSCF optimization, as well as the accuracy and stability of the valence excitation energies calculated within our spaces. We find high overlap of our orbitals with fully optimized CASSCF orbitals, demonstrating their high quality. We can also obtain good CASSCF excitation energies in cases where the excitations are dominated by valence correlation. In molecules where the excitations
are not of this character, we find that the addition of dynamic correlation (through the $N$-electron valence perturbation theory) yields quantitative agreement with experiment.

No doubt it will still be necessary to experiment with active spaces in the modeling of large and very complex molecules. Our study provides two reasons to believe that the difficulty of performing reliable multireference calculations in complex problems can be reduced using the AVAS technique. First, the simple procedure makes it trivial to obtain not only the minimal active spaces, but also extended active spaces, for example, including additional ligand orbitals. This makes it simpler to systematically explore different active spaces, eliminating user error and subjectivity in their definition, and allowing for convergence of properties with respect to the active space size. Second, systematically varying active space size, while including a dynamic correlation treatment (such as NEVPT2) provides a straightforward way to assess whether our active space is converged, as computed observables should become insensitive to the active space size. For these reasons, we believe that the AVAS construction provides a simple route to painless multireference calculations by non-experts, particularly in complex systems involving transition metals.

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REFERENCES


