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On the invariance of the configuration interaction energy with respect to orbital rotations

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Summary. The invariance of the configuration interaction (CI) energy with respect to orbital rotation is considered. The inclusion of all spin couplings versus only those from the first-order interacting space is considered. A definition for the analog of a second-order CI calculation when inactive electrons are present is proposed.

Key words: Configuration interaction energy – CI – Invariance – Orbital rotations

The energy of a configuration interaction (CI) wave function that includes all single and double excitations from a single closed shell reference is invariant to the rotation of equivalent orbitals. That is, the energy is unchanged by a rotation of the virtual orbitals or by a rotation of the occupied orbitals. For open-shell CI calculations, however, the invariance properties are less well known. The lack of invariance introduces additional terms that complicate the gradient evaluation (see for example Ref. [1]) and can cause problems even when only the energy is required. For example, we recently [2] encountered difficulties in determining the potential energy for the NH $^5\Sigma^-$ state at long range. The orbitals were optimized using a complete active space self-consistent field (CASSCF) procedure with the N $2p$ and H $1s$ orbitals in the active space. Note this wave function contains a single configuration state function (CSF) and is therefore equivalent to an SCF treatment. Thus, the two active σ orbitals (the N $2p\sigma$ and H $1s$) have occupations of one and can mix arbitrarily when the CASSCF natural orbitals are obtained. In a subsequent single-reference singles and doubles CI calculation, the N $2s$ electrons were also correlated and the mixing of the active orbitals led to an irregular potential that was obviously incorrect; the energy at r_e could vary by 28 cm^{-1} with the choice of orbitals for a potential with a well depth of 10 cm^{-1}. To obtain CI energies that were invariant to this rotation, the CI was expanded by adding the N $2s$ orbital to the CI active space. While the solution was straightforward for this case, the question remains of how to generate a consistent definition of the CI expansion when orbital invariance is important.

First, consider the case of a six-electron triplet, where the CI expansion consists of all single and double excitations from the reference:

$$a^2b^2c\alpha d\alpha. \tag{1}$$

If the CI expansion is obtained by including all spin couplings for each occupation that can be generated, then the energy is invariant to the mixing of the virtual orbitals and to the mixing of the inactive orbitals a and b. The energy is, however, not invariant to the rotation of active orbitals c and d. The lack of invariance of the energy with respect to the rotation of the active (open-shell) orbitals can be demonstrated by considering the excitation $b^2 \rightarrow ef$. When orbitals e and f are triplet coupled, orbitals c and d must be singlet coupled. Thus, for the energy to be invariant to the mixing of orbitals c and d:

$$a^2c^2e\alpha f\alpha \tag{2}$$

and

$$a^2d^2e\alpha f\alpha \tag{3}$$

are required. However, these configurations are not included in the CI expansion because they differ from the reference (1) by three spatial orbitals. The configurations required to restore the invariance of the energy can be obtained by including two additional references:

$$a^2b^2c^2 \tag{4}$$

and

$$a^2b^2d^2. \tag{5}$$

Note, however that the configurations in (4) and (5) do not have the same spin multiplicity as that in (1), and these configurations are not included in the CI expansion; only those configurations of the correct spin multiplicity that can be generated by single and double excitations from them are included.

The lack of invariance of the energy can also be eliminated by restricting the spin couplings to those of the first-order interacting space [3] rather than including all spin couplings for a given number of open-shell orbitals. Considering our example, the triplet coupling of orbitals e and f would be excluded for the $b^2 \rightarrow ef$ excitation. While this configuration differs from the reference by two spatial orbitals, it differs by three spin-orbitals and therefore has a matrix element of zero with the reference. Thus this configuration and all others that lead to the lack of energy invariance are excluded when the interacting space is used.

The lack of invariance of the energy with respect to orbital rotation may not cause any problems. For example, if an SCF approach is used to optimize the orbitals, the open-shell orbitals are commonly defined as eigenvectors of an appropriate Fock operator. Thus unless their orbital energies are essentially degenerate, the orbitals vary smoothly across a surface and so will the CI energy. If a CASSCF approach is used to optimize the orbitals, obvious problems at the CI level will only arise if similar natural orbital occupation numbers lead to an arbitrary mixing of the active orbitals, as was the case in our NH example.

A CASSCF/multireference CI (MRCI) procedure that uses only selected reference configurations is generally not invariant to the rotation of the active orbitals. Even a CI calculation that includes all of the configurations in the CASSCF as references (CAS-ref CI) is not necessarily invariant as we saw in our above example. This includes the case where there are no inactive orbitals when spatial symmetry is used to eliminate reference configurations. For example, consider a $^3A_1$ state with six electrons correlated and an active space that consists of two a_1, one b_1, one b_2 and one a_2 orbital, giving the nine reference configurations in Table 1. For invariance of the energy to rotation of the $1a_1$ and $2a_1$ orbitals, configurations such as:

$$1a_1^2 1b_1^2 e\alpha f\alpha \tag{6}$$

and

$$2a_1^2 1b_1^2 e\alpha f\alpha \tag{7}$$

are required in the CI expansion, because:

$$1a_1^1 2a_1^1 1b_1^2 e\alpha f\alpha \tag{8}$$

is generated by a double excitation from the reference configurations. However, the configurations in (6) and (7) are not generated by a single or double excitation from one of the nine CASSCF reference configurations. Thus, it is necessary to impose the interacting space restriction or to include additional references. It should be noted that it may not be possible to implement the true first-order interacting space for arbitrary references in some direct CI programs because of restrictions on the spin couplings.

A second-order CI (SOCI) expansion [4] consists of all configuration with n electrons in the active orbitals, $n-1$ electrons in the active orbitals and one electron in the virtual orbitals, and $n-2$ electrons in the active orbitals and two electrons in the virtual orbitals. This is equivalent to all single and double excitations of the desired spatial symmetry that can be generated from the CASSCF wave functions of all possible spatial symmetries (having the correct number of active orbitals and electrons). Thus, in the case of no spatial symmetry, the SOCI and the CAS-ref CI are equivalent. The SOCI has the feature that the energy is invariant to rotation of the active and to the rotation of the virtual orbitals. Thus in our example, configurations of the type shown in (6) and (7) would be generated. For prototype direct CI programs that trace their origin to the unitary group formulation, it is simple to extend them to include the extra references of the wrong spatial symmetry.

In many cases, the number of active orbitals and electrons must be restricted to keep the CASSCF tractable. Thus the number of electrons correlated in the

Table 1. The 5(9) reference occupations (CSFs) in the $^3A_1$ CAS-ref CI calculation with 6 electrons and two active a_1, one b_1, one b_2, and one a_2 orbital

		Orbital occupation				
	# CSF[a]	$1a_1$	$2a_1$	$1b_1$	$1b_2$	$1a_2$
1	1	1	1	2	2	0
2	1	1	1	2	0	2
3	1	1	1	0	2	2
4	3	2	1	1	1	1
5	3	1	2	1	1	1

[a] The number of CSFs arising from a given occupation

subsequent CI calculation will be larger than the number of active electrons in the CASSCF calculation. In general, the CI energy will not be invariant to rotation of the active orbitals if the CI expansion consists of all single and double excitations from the CASSCF, even if excitations from the CASSCF wave functions of the wrong spatial symmetry are included as reference configurations. For a system with m inactive and n active electrons, invariance of the energy with respect to active orbital rotation is obtained if the CI expansion consists of the excitations defined in Table 2. This expansion consists of all single and double excitations from the CASSCF calculation of the desired spin multiplicity and spatial symmetry, as well as all single and double excitations from the CASSCF wave functions having the wrong spin multiplicity and spatial symmetry. These configurations can be generated with a minor modification to our direct CI program. The energy of this wave function is invariant with respect to rotation of the inactive, active, or virtual orbitals. Because this wave function has the desirable feature of having the energy invariant to mixing of the equivalent orbitals, we suggest this as the definition of a SOCI calculation when there are inactive electrons. We should also note that this definition is similar to that used in the restricted-active-space (RASSCF) wave function [5], where the RAS1, RAS2, and RAS3 spaces are equivalent to the inactive, active, and virtual orbitals, respectively.

While the SOCI procedure has the desirable feature of the invariance of the energy with respect to orbital rotations, it can result in very long CI expansions; In some cases becoming prohibitively long. Even using the CAS-ref with the interacting space approach might result in a prohibitively long CI expansion. In a study of symmetry breaking, another application where the invariance of the energy with respect to orbital rotation is important, McLean et al. [6] divided the active space into subspaces, and then by defining the CI expansion using distributions analogous to those in Table 2 achieved a selected reference MRCI with well defined properties for the energy with respect to orbital rotation.

In addition to the calculation of gradients, there are other cases where the invariance of the energy with respect to orbital rotation can be useful. Consider the case of several weakly bound states arising from the same asymptote, for example, the four states ($^3\Delta$, $^3\Pi$, $^3\Sigma^-$ and $^3\Phi$) of CoHe^+ arising from the ground state ($^3F + {}^1S$) asymptote. If a state-averaged CASSCF procedure is used to optimize all states (weighted by their orbital degeneracy) derived from a given asymptote, the asymptotic energy of all states will be identical. However, if a

Table 2. The distributions of electrons defining an SOCI with inactive electrons

inactive	active	virtual
m	n	0
m	$n-1$	1
m	$n-2$	2
$m-1$	$n+1$	0
$m-1$	n	1
$m-2$	$n+2$	0
$m-2$	$n+1$	1
$m-2$	n	2
$m-1$	$n-1$	2

CAS-ref CI procedure is used the CI energies will not agree at infinite separation. While it is probably acceptable to shift all the potentials into agreement at infinite separation [7], a CASSCF/SOCI treatment yields CI energies that all agree at long range, hence eliminating one uncertainty from the calculation.

Problems at the CI level can also arise when studying a molecule with higher symmetry than used in the calculation. Consider the $^2E(e^3)$ state of molecule with C_{3v} symmetry, but where the calculation is performed in C_s symmetry. Even if the orbitals have the full symmetry, the $^2A'(e_x^1e_y^2)$ component of the ^2E state will not necessarily have the same energy as the $^2A''(e_x^2e_y^1)$ component. If the CI wave functions includes all single and double excitations away from both occupations, the energies will agree. However, in each CI calculation one of the references has the wrong spatial symmetry and therefore the first-order interacting space can not be used. This is essentially the same problem as for $CoHe^+$, where to bring all asymptotic energies into agreement, a SOCI calculation is required to treat all components of the Co^+ ^3F state equivalently.

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