CFG CIPSI

Vijay Gopal Chilkuri (vijay.gopal.c@gmail.com)

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Contents

1 Theoretical background

Here we describe the main theoretical background and definitions of the Configuration (CFG) based CIPSI algorithm. The outline of the document is as follows. First, we give some definitions of the CFG many-particle basis follwed by the definitions of the overlap, one-particle, and two-particle matrix-elements. Finally, an algorithm is presented for the sigma-vector (

$$\sigma$$

-vector defined later) calculation using the CFG basis.

- Definitino of CI basis

  In CFG based CIPSI, the wavefunction is represented in CFG basis as shown in Eq:

  1

  .

  $$|\psi\rangle = \sum_{ij} c_{ij}^{s} |\phi_i^j\rangle \tag{1}$$

  where the

  $$|\Phi_i^j\rangle$$

represent Configuration State Functions (CSFs) which are expanded in terms of Bonded functions (BFs) as shown in Eq:

2

.

$$|\Phi_i^j\rangle = \sum_{i,k}^{j} O_{i,k}^j \, |^S\phi_k(i,j)\rangle \tag{2}$$

Where the functions

$$|^S\phi_k(i,j)\rangle$$

represent the BFs for the CFG

$$i$$

. Each CFG contains a list of CSFs related to it which describes the spin part of the wavefunction (see Eq:~3) which is encoded in the BFs as shown below in Eq:~**??**.

$$|^S\Phi_i\rangle = \left\{|^S\Phi_i^1\rangle, |^S\Phi_i^2\rangle, \ldots, |^s\phi_i^{n_{csf}}\rangle\right. \tag{3}$$

$$|^s\phi_i\rangle = \left\{c_i^1, c_i^1, \ldots, c_i^{N_{CSF}}\right\} \tag{4}$$

Each of the CSFs belonging to the CFG

$$|^S\Phi_i\rangle$$

have coefficients associated to them as shown in Eq:~5. Crucially, the bonded functions defined in Eq:~**??** are not northogonal to each other.

$$|^S\phi_k(i,j)\rangle = (i\bar{i})\ldots(j,k)lm \tag{5}$$

The bonded functions are made up of products of slater determinants. There are three types of determinants, first, the closed shell pairs

$$(i\bar{i})$$

. Second, the open-shell singlet pairs

$$(i,j)$$

which are expanded as

$$(i,j) = \frac{|i\bar{j}\rangle - |\bar{i}j\rangle}{\sqrt{2}}$$

. Third, the open-shell SOMOs which are coupled parallel and account for the total spin of the wavefunction

$$(l(m\ldots$$

. They are shown as open brackets.

- Overlap of the wavefunction

  Once the wavefunction has been expanded in terms of the CSFs, the most fundamental operation is to calculate the overlap between two states. The overlap in the basis of CSFs is defined as shown in Eq:˜6.

$$\langle {}^S\Phi_i | {}^S\Phi_j \rangle = \sum_{kl} C_i C_j \langle {}^S\Psi_i^k | {}^S\Psi_j^l \rangle \tag{6}$$

  Where the sum is over the CSFs

$$k$$

  and

$$l$$

  corresponding to the

$$i$$

  and

$$j$$

  CFGs respectively. The overlap between the CSFs can be expanded in terms of the BFs using the definition given in Eq:˜2 and Eq:˜3 as given in Eq:˜7.

$$\langle {}^S\Phi_i^k | {}^S\Phi_j^l \rangle = \sum_m \sum_n \left(O_{i,m}^k \right)^\dagger \langle {}^S\phi_m(i,k) | {}^S\phi_n(j,l) \rangle \, O_{j,n}^l \tag{7}$$

  Therefore, the overlap between two CSFs can be expanded in terms of the overlap between the constituent BFs. The overlap matrix

$$S_{mn}$$

is of dimension

$$\left(N^k_{N_{BF}}, N^l_{N_{BF}}\right)$$

. The equation shown above (Eq:˜7) can be written in marix-form as shown below in Eq:˜8.

$$\langle {}^S\Phi_i | {}^S\Phi_j \rangle = (C_{i,1})^\dagger \, \mathbf{O}_i \cdot \mathbf{S}_{ij} \cdot \mathbf{O}_j C_{j,1} \tag{8}$$

Note that the overlap between two CFGs does not depend on the orbital labels. It only depends on the number of Singly Occupied Molecular Orbitals (SOMOs) therefore it can be pretabulated. Actually, it is possible to redefine the CSFs in terms of a linear combination of BFs such that

$$S_{ij}$$

becomes the identity matrix. In this case, one needs to store the orthogonalization matrix

$$\tilde{\mathbf{O}}_i$$

which is given by

$$\mathbf{O}_i \cdot S_i^{1/2}$$

for a given CFG

$$i$$

. Note that the a CFG

$$i$$

is by definition of an orthonormal set of MOs automatically orthogonal to a CFG

$$j$$

with a different occupation.

- Definition of matrix-elements

  The matrix-element (ME) evaluation follows a similar logic.