

CFG CIPSI

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1 Biblio

2 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 followed by the definitions of the overlap, one-particle, and two-particle matrix-elements. Finally, an algorithm is presented for the sigma-vector (σ -vector defined later) calculation using the CFG basis.

2.1 Definitinon of CI basis

In CFG based CIPSI, the wavefunction is represented in CFG basis as shown in Eq: 1.

$$|\Psi\rangle = \sum_{i=1}^{N_{\text{CFG}}} \sum_{j=1}^{N_{\text{CSF}}(i)} c_{ij}^S |\Phi_i^j\rangle \quad (1)$$

where the $|\Phi_i^j\rangle$ represent Configuration State Functions (CSFs) which are expanded in terms of Bonded functions (BFs) as shown in 2.

$$|\Phi_i^j\rangle = \sum_k O_{kj}^{N_{\text{SOMO}}(i)} |^S\phi_k(i, j)\rangle \quad (2)$$

where the functions $|^S\phi_k(i, j)\rangle$ represent the BFs for the CFG $|^S\Phi_i\rangle$. The coefficients $O_{a,k}^b$ depend only on the number of SOMOs in Φ_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: 5.

$$|^S\Phi_i\rangle = \left\{ |^S\Phi_i^1\rangle, |^S\Phi_i^2\rangle, \dots, |^s\Phi_i^{N_{\text{CSF}}}\rangle \right\} \quad (3)$$

$$\mathbf{c}_i = \left\{ c_i^1, c_i^2, \dots, c_i^{N_{\text{CSF}}} \right\} \quad (4)$$

Each of the CSFs belonging to the CFG $|^S\Phi_i\rangle$ have coefficients associated to them as shown in Eq: 4. Crucially, the bonded functions defined in Eq: 5 are not northogonal to each other.

$$|^S\phi_k(i, j)\rangle = (a\bar{a}) \dots (b\ c)(d(e \quad (5)$$

i is the index of the CFG and j determines the coupling.

The bonded functions are made up of products of slater determinants. There are three types of determinants, first, the closed shell pairs $(a\bar{a})$. Second, the open-shell singlet pairs $(b\ c)$ which are expanded as $(b\ c) = \frac{|bc\rangle - |\bar{b}\bar{c}\rangle}{\sqrt{2}}$. Third, the open-shell SOMOs which are coupled parallel and account for the total spin of the wavefunction ($l(m \dots$. They are shown as open brackets.

2.2 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.

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

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.

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

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 $\left(N_{NBF}^k, N_{NBF}^l \right)$. The equation shown above (Eq: 7) can be written in matrix-form as shown below in Eq: 8.

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

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.

2.3 Definition of matrix-elements

The matrix-element (ME) evaluation follows a similar logic as the evaluation of the overlap. However, here the metric is the one-, or two-particle operator \hat{E}_{pq} or $\hat{E}_{pq}\hat{E}_{rs}$ as shown in Eq: 9 and Eq: 10.

$$\langle {}^S\Phi_i^k | \hat{O}_{pq} | {}^S\Phi_j^l \rangle = (C_{i,1})^\dagger \mathbf{O}_i \cdot \mathbf{A}_{ij}^{pq} \cdot \mathbf{O}_j C_{j,1} \quad (9)$$

$$\langle {}^S\Phi_i^k | \hat{O}_{pq,rs} | {}^S\Phi_j^l \rangle = \sum_K (C_{i,1})^\dagger \mathbf{O}_i \cdot \mathbf{A}_{ik}^{pq} \cdot \mathbf{O}_k \mathbf{O}_k \cdot \mathbf{A}_{kj}^{rs} \cdot \mathbf{O}_j C_{j,1} \quad (10)$$

Where, \hat{O}_{pq} and $hatO_{pq,rs}$ represent an arbitrary one-, and two-particle operators respectively. Importantly, the one-, and two-particle matrix-element evaluation can be recast into an efficient matrix multiplication form which is crucial for a fast evaluation of the action of the operators \hat{O}_{pq} and $hatO_{pq,rs}$. The matrix \mathbf{A}_{ij}^{pq} contains the result of the operation $\langle {}^S\Phi_i^k | \hat{O}_{pq} | {}^S\Phi_j^l \rangle$ in terms of BFs and is therefore of size $NCSF(i) \times NBF(i)$. In this formulation, the determinant basis is entirely avoided. Note that the size and contents of the matrix \mathbf{A}_{ij}^{pq} depends only on the total number of SOMOs and the total spin

S , therefore, an optimal prototyping scheme can be devised for a rapid calculation of these matrix contractions. The resolution of identity (RI) is used to evaluate the two-particle operator since this alleviates the necessity to explicitly construct two-particle matrix-elements $\langle {}^S\Phi_i^k | \hat{O}_{pq,rs} | {}^S\Phi_j^l \rangle$ directly.

2.4 Sigma-vector evaluation

Once the \mathbf{A}_{ij}^{pq} matrices have been constructed for the given selected list of CFGs, the prototype lists for the \mathbf{A}_{ij}^{pq} matrices can be constructed. Following this, one can proceed to the evaluation of the sigma-vector as defined in the Eq 11.

$$\sigma = \sum_{pq} \tilde{h}_{pq} \hat{E}_{pq} | {}^S\Phi_j^l \rangle + \frac{1}{2} \sum_{pq,rs} g_{pq,rs} \hat{E}_{pq} \hat{E}_{rs} | {}^S\Phi_j^l \rangle \quad (11)$$

The one-electron part of the sigma-vector can be calculated as shown in Eq: 9 and the two-electron part can be calculated using the RI as shown in Eq: 10. The most expensive part involves the two-particle operator as shown on the RHS of Eq: 11. In this CFG formulation, the cost intensive part of the sigma-vector evaluation has been recast into an efficient BLAS matrix multiplication operation. Therefore, this formulation is the most efficient albeit at the cost of storing the prototype matrices \mathbf{A}_{ij}^{pq} . However, where the total spin is small and the largest number of SOMOs does not exceed 14, the \mathbf{A}_{ij}^{pq} matrices can be stored in memory.