

The most time consuming step in the ADC(2) calculation is definitely the construction of the so-called  $\sigma$ -vector, defined as

$$\sigma(\omega)^{(I)} = \mathbf{A}(\omega)\mathbf{b}^I$$

for the  $I$ -th root. Due to the eigenvalue dependence of the effective response matrix,  $\mathbf{A}$  has to be diagonalized for each excited state till the convergence of the excitation energy is achieved. The explicit form of the  $\sigma$ -vector is presented in the Table below. The non-iterative excitation energy, which can be calculated in a very similar fashion to the doubles correction of CIS(D) energy, is written as

$$\omega^{\text{Non-Iterative}} = \mathbf{X}_{\text{CIS}}^{(I)} \cdot \mathbf{A}(\omega^{\text{CIS}})\mathbf{X}_{\text{CIS}}^{(I)}$$

for  $I$ -th excited state. In this code, as a preliminary step the CIS equation is solved in order to generate the guess energy and vectors for use in the simultaneously expansion method (SEM). So, the non-iterative correction can be calculated as a  $I$ -th diagonal element of the Davidson mini-Hamiltonian at the first iteration.

Table: The  $\sigma$ -equation and intermediate tensors for ADC(2) model.

Nature	Formula
Amplitude	$K_{iajb} \leftarrow \frac{2(ia jb) - (ib ja)}{F_{ii} + F_{aa} - F_{jj} - F_{bb}}$
DC	$X_{ij} \leftarrow \sum_{kab} K_{iakb}(ja kb)$
DC	$X_{ab} \leftarrow \sum_{ijc} K_{iajc}(ib jc)$
DC+CIS	$A_{iajb} \leftarrow \delta_{ij}\delta_{ab}(F_{aa} - F_{ii}) + 2(ia jb) - (ij ab) - \frac{1}{2}(1 + P_{ia}P_{jb})\delta_{ij}(X_{ab}^t + X_{ab})$
DC	$D_{ia} \leftarrow \sum_{jb}(2(ia jb) - (ib ja))b_{jb}$
DC	$E_{ia} \leftarrow \sum_{jb} K_{iajb}b_{jb}$
DC	$\sigma_{ia} \leftarrow \frac{1}{2} \sum_{jb} K_{iajb}D_{jb}$
DC	$\sigma_{ia} \leftarrow \frac{1}{2} \sum_{jb}(2(ia jb) - (ib ja))E_{jb}$
OR	$Z_{iajb} \leftarrow \sum_c b_{ic}(ja cb)$
OR	$Z_{iajb} \leftarrow - \sum_k (ia jk)b_{kb}$
OR	$B_{iajb} \leftarrow \frac{2Z_{iajb} - Z_{ibja} + 2Z_{jbja} - Z_{jaib}}{\omega + F_{ii} - F_{aa} + F_{jj} - F_{bb}}$
OR	$\sigma_{ia} \leftarrow \sum_{jbc} B_{jcib}(jc ab)$
OR	$\sigma_{ia} \leftarrow \sum_{jkb}(ji kb)B_{jakb}$