Tensorial Equations for the ADC(2) model

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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

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

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 simultaneous 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+ADC(1) | $A_{iajb} \leftarrow \delta_{ij}\delta_{ab}(F_{aa} - F_{ii}) + 2(ia\|jb) - (ij\|ab) - \frac{1}{2}(1 + P_{ia}P_{jb})\delta_{ij}(X^t_{ab} + X_{ab})$ |
| 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 | $B_{iajb} \leftarrow \frac{2Z_{iajb}-Z_{ibja}+2Z_{jbia}-Z_{jaib}}{\omega+F_{ii}-F_{aa}+F_{jj}-F_{bb}}$ |
| OR | $\sigma_{ia} \leftarrow \sum_{jbc} B_{jcib}(jc\|ab)$ |
| OR | $\sigma_{ia} \leftarrow -\sum_{jkb}(ji\|kb)B_{jakb}$ |