Double-excited states
(NOSE Implementation White Paper 2, ver. 1.0)

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Abstract

This paper describes details of treatment of two-exciton and double-excitation states in NOSE.

1 Basic terms and theoretical background

The term double-excited states referes to an arbitrary quantum mechanical states of a composed system (aggregate) which contains more than two two-level (or multi-level) entities (chromophores) which can be excited from the ground state. States of the aggregate that correspond to two such entities excited are refered to here as double-excited states. In NOSE and related papers, we refere to a double-excited eigenstates of the aggregate as to a two-exciton state, while to term double-excitation state referes to a state corresponding to two excitations localized on two-individual chromophores.

1.1 Two-excitation line-shape function

In the double-excitation basis the treatment of the line-shape function is relatively simple. By generalization of the single-excitation line-shape function we get

$$g_{NM}(t) = \frac{1}{\hbar^2} \int_0^t d\tau \int_0^\tau d\tau' \langle \Delta V_N(t) \Delta V_M(0) \rho_{eq} \rangle. \tag{1}$$

Here for the double-excitation energy gap holds

$$\Delta V_N(t) \equiv \Delta V_{(m,n)}(t) = \Delta V_m(t) + \Delta V_n(t), \tag{2}$$

and consequently we have

$$g_{NM}(t) \equiv g_{(n,m)(k,l)}(t) = g_{nk}(t) + g_{nl}(t) + g_{mk}(t) + g_{ml}(t). \tag{3}$$

In the recent version of NOSE, we expect that the correlation of the fluctuations on different molecules is entirely uncorrelated, i.e.

$$g_{ab}(t) = \delta_{ab} g_{aa}(t). \tag{4}$$

This yields

$$g_{(n,m)(k,l)}(t) = (\delta_{nk} + \delta_{nl})g_{nn}(t) + (\delta_{mk} + \delta_{ml})g_{mm}(t). \tag{5}$$

2 Implementation details

2.1 Conversion between indices

Often we need a conversion between indices of single- and double-excitation states. Each double-excitation state is composed of exactly two single-excitation states, and correspondingly, each double index N corresponds to two single indices m and n and vice versa. The conversion should correspond to the following chunk of code

```
I = 0
do m = 1, N1
  do n = m+1, N1
     I = I + 1
     print *, I, ' <-> (', m,n,')'
  end do
end do
```