

Multistate Hylleraas type equation for rotated functions  $|\tilde{N}\rangle$ :

$$E_L^{(2)} = \sum_{\Omega\Omega'} \sum_{MN} \langle \tilde{M} | \hat{T}_{\Omega',ML}^\dagger (\hat{f} - E_L^{(f)}) \hat{T}_{\Omega,LN} | \tilde{N} \rangle + \langle \tilde{M} | \hat{T}_{\Omega',ML}^\dagger \hat{H} | \tilde{N} \rangle. \quad (1)$$

Differentiate with respect to T-amplitude,  $T_{\Omega',ML}^\dagger$ , to get amplitude equation:

$$\frac{\partial E_L^{(2)}}{\partial T_{\Omega',ML}^\dagger} = \sum_{\Omega} \sum_N \langle \tilde{M} | \hat{E}_{\Omega'}^\dagger (\hat{f} - E_L^{(f)}) \hat{T}_{\Omega,LN} | \tilde{N} \rangle + \langle \tilde{M} | \hat{E}_{\Omega'}^\dagger \hat{H} | \tilde{N} \rangle = 0 \quad (2)$$

Left hand side should be stationary with respect to variations in T-amplitudes, in other words, we should minimize the residual  $r_{LN,\Omega}$ ,

$$r_{LN,\Omega}[T_{\Omega,LN}] = \langle \tilde{M} | \hat{E}_{\Omega'}^\dagger (\hat{f} - E_L^{(f)}) \hat{T}_{\Omega,LN} | \tilde{N} \rangle = 0, \quad (3)$$

with respect to variations in  $T_{\Omega,LN}$ ;

$$r_{LN,\Omega}[T_{\Omega,LN}] = r_{LN,\Omega}[T_{\Omega,LN} + \Delta T_{\Omega,LN}] \quad (4)$$

$$r_{LN,\Omega}[T_{\Omega,LN}] = r_{LN,\Omega}[T_{\Omega,LN}] - \langle \tilde{M} | \hat{E}_{\Omega'}^\dagger (\hat{f} - E_L^{(f)}) \Delta T_{\Omega,LN} \hat{E}_{\Omega} | \tilde{N} \rangle \quad (5)$$

leading to

$$\frac{r_{LN,\Omega}[T_{\Omega,LN}]}{(r_{LN,\Omega}[T_{\Omega,LN}] - \langle \tilde{M} | \hat{E}_{\Omega'}^\dagger (\hat{f} - E_L^{(f)}) \hat{E}_{\Omega} | \tilde{N} \rangle \Delta T_{\Omega,LN})} = 1 \quad (6)$$

assuming we are not too far from convergence

$$r_{LN,\Omega}[T_{\Omega,LN}] \ll \langle \tilde{M} | \hat{E}_{\Omega'}^\dagger (\hat{f} - E_L^{(f)}) \hat{E}_{\Omega} | \tilde{N} \rangle \Delta T_{\Omega,LN} \quad (7)$$

so

$$\Delta T_{\Omega,LN} \approx \frac{r_{LN,\Omega}[T_{\Omega,LN}]}{\langle \tilde{M} | \hat{E}_{\Omega'}^\dagger (\hat{f} - E_L^{(f)}) \hat{E}_{\Omega} | \tilde{N} \rangle}. \quad (8)$$

The states  $\{|\tilde{N}\rangle\}$  diagonalize the Fock operator, hence  $M = N$ . Furthermore, the off diagonal elements of the Fock operator (in terms of molecular orbital indexes) are small, so we need only consider terms where  $\Omega = \Omega'$ . This leads to

$$\Delta T_{\Omega,LN} \approx \frac{r_{LN,\Omega}[T_{\Omega,LN}]}{\langle \tilde{N} | \hat{E}_{\Omega}^\dagger (\hat{f} - E_L^{(f)}) \hat{E}_{\Omega} | \tilde{N} \rangle}. \quad (9)$$