The distinguishable cluster

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The standard way to improve a CC calculation

Reaching full CI

CCD $\rightarrow$ CCSD $\rightarrow$ CCSD(T) $\rightarrow$ CCSDT $\rightarrow$ CCSDTQ $\rightarrow$ *etc*

CCSD(T) already scales as $O(N^7)$ with N the number of spin-orbital in the basis set.

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Another idea

"Addition by substraction"

For other examples of such methods see for example: Huntington and Nooijen JCP 133 (2010) 184109, Scuseria *et al.* JCP 139 (2013) 104113 ...

Communication: The distinguishable cluster approximation

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Daniel Kats, and Frederick R. Manby

The CCD equations

The energy equation

$$\Delta E_{CCD} = \langle 0|\hat{H}_{\mathrm{N}}\hat{T}_2|0\rangle \tag{1}$$

$$\Delta E_{CCD} = \frac{1}{4}\sum_{ijab} \langle ij||ab\rangle \, t_{ij}^{ab} \tag{2}$$

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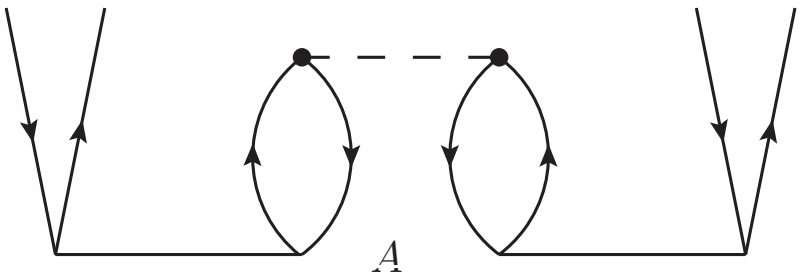
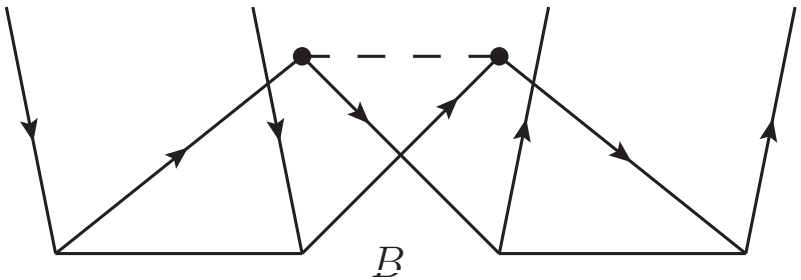
The amplitude equations

$$0 = \left\langle \phi_{ij}^{ab} \middle| (\hat{H}_{\mathrm{N}}(1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2^2))_c \middle| 0 \right\rangle \tag{3}$$

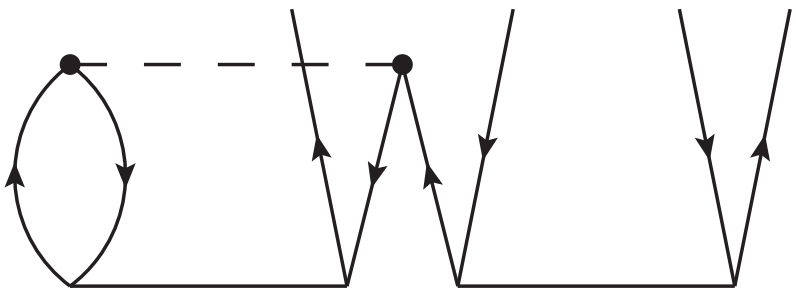
The quadratic diagrams of the CCD amplitude equations



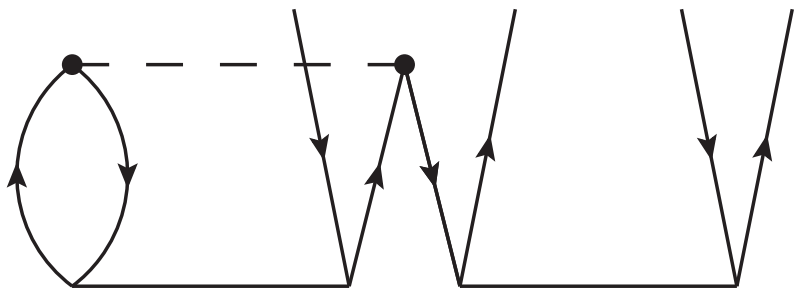
A



B

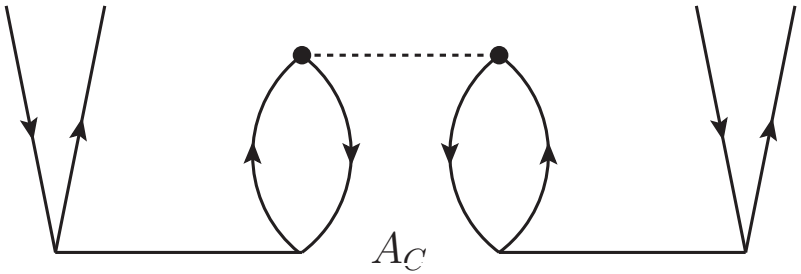


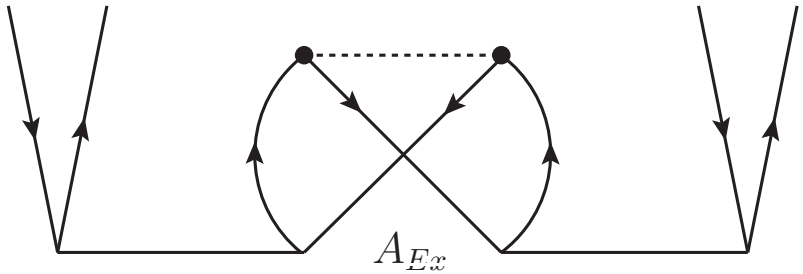
C



D

The two-electron case





In the two-electron case we have the relations:

$$A_{Ex} + \frac{C}{2} = 0 \quad \text{and} \quad B + \frac{D}{2} = 0$$

Hence the amplitude equations can be written in the form:

$$0 = A_C + \frac{C}{2} + \frac{D}{2}$$

The algebraic DCD amplitude equation

You can find the CCD and the DCD equations in Rishi's 2016 paper.

The N_2 dissociation curve

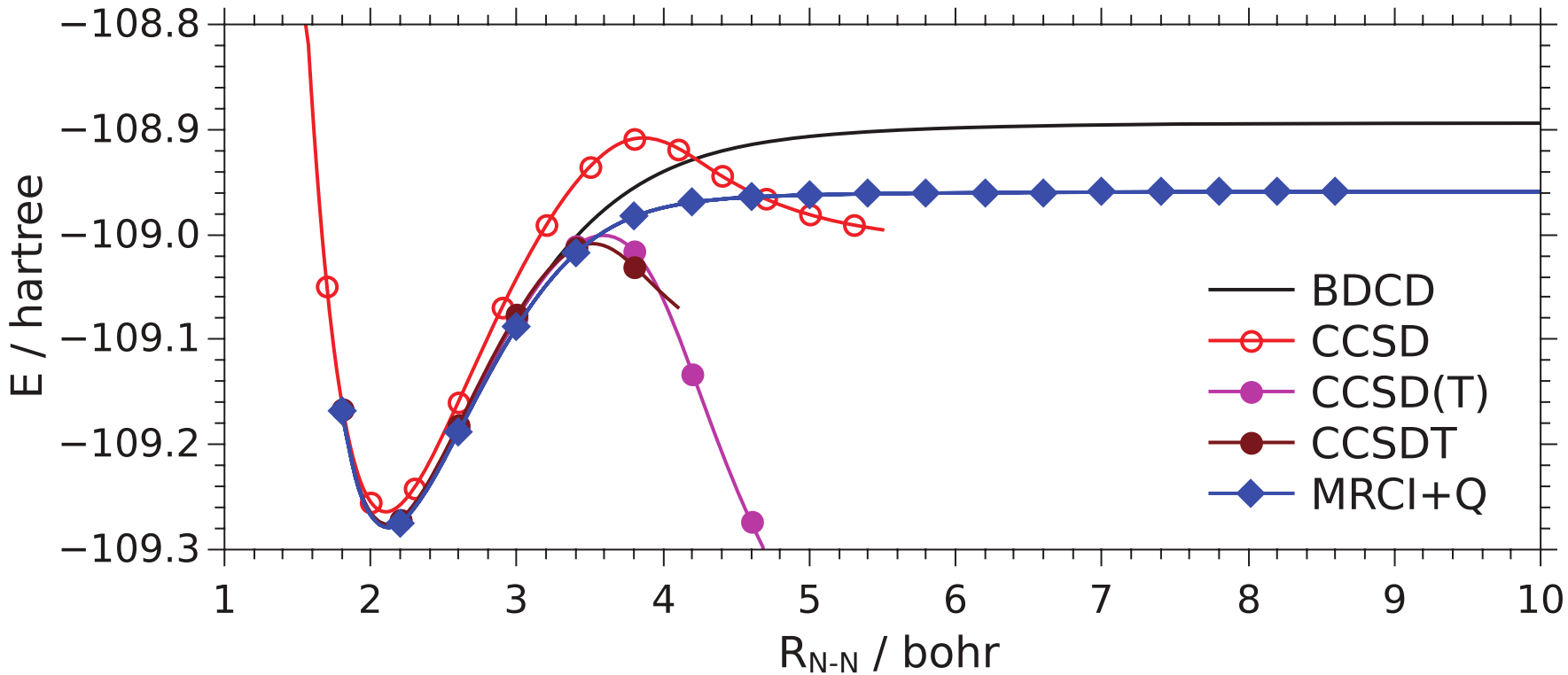


FIG. 2. Potential energy curves for N_2 dissociation.

Some further studies

- The effect of orbital relaxation on DCD: D. Kats JCP 141 (2014) 061101
- Explicitly correlated DC: D. Kats *et al.* JCP 142 (2015) 064111
- The (T) correction for DC: D. Kats JCP 144 (2016) 044102
- Extensive study of the N_2 disscoiation process: Rishi, Perera and Bartlett JCP 144 (2016) 124117