The ring Coupled-Cluster

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4th December 2020

Algebraic CCD equation

$$
\begin{aligned}
0 = \; & \langle ij||ab\rangle + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - f_i^k t_{kj}^{ab} - f_j^k t_{ik}^{ab} && \}\text{Driver} \\
& + \frac{1}{2} \langle ab||cd\rangle \, t_{ij}^{cd} + \frac{1}{2} \langle ij||kl\rangle \, t_{kl}^{ab} + \frac{1}{4} t_{kl}^{ab} \langle cd||kl\rangle \, t_{ij}^{cd} && \}\text{Ladder} \\
& + t_{ik}^{ac} \langle cj||kb\rangle + t_{kj}^{cb} \langle ci||ka\rangle + \langle cd||kl\rangle \, t_{ik}^{ac} t_{lj}^{db} && \}\text{Ring} \\
& - t_{ik}^{bc} \langle cj||ka\rangle - t_{kj}^{ca} \langle ci||kb\rangle - \langle cd||kl\rangle \, t_{lj}^{ad} t_{ik}^{cb} && \}\text{Crossed-ring} \\
& + \frac{1}{2} \hat{P}_{ij,ab} \langle cd||kl\rangle \, t_{ik}^{ac} t_{lj}^{db} && \}\text{Mosaic}
\end{aligned}
$$

Ring Coupled-Cluster Double

$$
\begin{aligned}
0 = &\ \langle ij||ab\rangle + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - f_i^k t_{kj}^{ab} - f_j^k t_{ik}^{ab} \}\text{Driver} \\
&+ t_{ik}^{ac}\langle cj||kb\rangle + t_{kj}^{cb}\langle ci||ka\rangle + \langle cd||kl\rangle\, t_{ik}^{ac} t_{lj}^{db} \}\text{Ring}
\end{aligned} \tag{1}
$$

- The rCCD method results agree with the RPA results[1].
- Numerical proof of the equivalence[2].

[1] David L. Freeman (1977). "Coupled-Cluster Expansion Applied to the Electron Gas: Inclusion of Ring and Exchange Effects". In: *Phys. Rev. B* 15, pp. 5512–5521.

[2] G. Kresse and A. Grüneis, results presented at the XIV ESCMQC, Isola d'Elba, Italy, 3 October 2008 (unpublished).

The formal equivalence of RPAx and rCCD

AIP | The Journal of Chemical Physics

The ground state correlation energy of the random phase approximation from a ring coupled cluster doubles approach

Gustavo E. Scuseria, Thomas M. Henderson, and Danny C. Sorensen

The Random Phase Approximation[3]

The adiabatic-connection

$$E_c = \frac{1}{2}\int_0^1 \mathrm{d}\alpha \sum_{pq,rs} \langle rq|sp\rangle \left(\boldsymbol{P}_{c,\alpha}\right)_{pq,rs} q$$

The plasmon formula

$$E_c = \frac{1}{2}\sum_n (\omega_{1,n}^{RPA} - \omega_n^{TDA})$$

[3] János G. Ángyán et al. (2011). "Correlation Energy Expressions from the Adiabatic-Connection Fluctuation–Dissipation Theorem Approach". In: *J. Chem. Theory Comput.* 7, pp. 3116–3130.

The Random Phase Approximation

The fermionic Hamiltonian

$$H = h_{pq} a_p^\dagger a_q + \frac{1}{4} \langle pq || rs \rangle \, a_p^\dagger a_q^\dagger a_s a_r$$

The quasi-boson approximation

$$a_a^\dagger a_i \rightarrow b_\beta \text{ with}$$

$$[b_\beta, b_{\beta'}^\dagger] = \delta_{\beta\beta'} \text{ and } [b_\beta, b_{\beta'}] = 0 \; and \; [b_\beta^\dagger, b_{\beta'}^\dagger] = 0$$

The bosonic Hamiltonian

$$H = E_{\text{HF}} + \frac{1}{2} \begin{pmatrix} \boldsymbol{b}^\dagger & \boldsymbol{b} \end{pmatrix} \begin{pmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^* & \boldsymbol{A}^* \end{pmatrix} \begin{pmatrix} \boldsymbol{b} \\ \boldsymbol{b}^\dagger \end{pmatrix} - \frac{1}{2} \text{Tr}(\boldsymbol{A}) \text{ with}$$

$$A_{\beta\beta'} \rightarrow A_{jb,ia} = f_{ab}\delta_{ij} - f_{ij}\delta_{ab} + \langle aj || ib \rangle \text{ and } B_{\beta\beta'} \rightarrow B_{jb,ia} = \langle ij || ab \rangle$$

Ladder Coupled-Cluster Double

$$
\begin{aligned}
0 = &\ \langle ij||ab\rangle + f_c^a t_{ij}^{cb} + f_c^b t_{ij}^{ac} - f_i^k t_{kj}^{ab} - f_j^k t_{ik}^{ab} && \}\text{Driver} \\
&+ \frac{1}{2}\langle ab||cd\rangle\, t_{ij}^{cd} + \frac{1}{2}\langle ij||kl\rangle\, t_{kl}^{ab} + \frac{1}{4} t_{kl}^{ab}\langle cd||kl\rangle\, t_{ij}^{cd} && \}\text{Ladder}
\end{aligned}
$$

- Equivalent to pp-RPA, the formal proof in terms of general quasi-bosons is in Scuseria *et. al.* 2013[4].

[4] Gustavo E. Scuseria, Thomas M. Henderson, and Ireneusz W. Bulik (2013). "Particle-Particle and Quasiparticle Random Phase Approximations: Connections to Coupled Cluster Theory". In: *J. Chem. Phys.* 139, p. 104113.

Removal of the culprit terms: proof of concept[5]

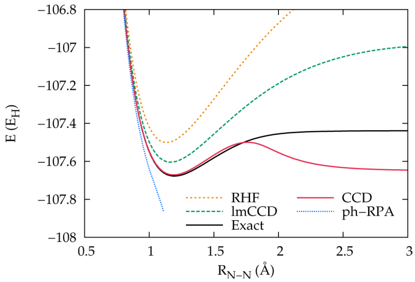

Figure 1: Total energies of the N_2 molecule in the STO-3G basis set as a function of bond length

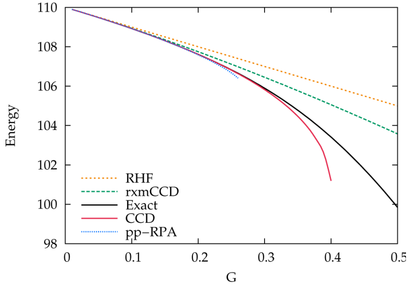

Figure 2: Total energies in the attractive pairing Hamiltonian as a function of interaction strength G

[5] Ireneusz W. Bulik, Thomas M. Henderson, and Gustavo E. Scuseria (2015). "Can Single-Reference Coupled Cluster Theory Describe Static Correlation?" In: *J. Chem. Theory Comput.* 11, pp. 3171–3179.

Effect of the mosaic terms

- Thermodynamic limit of the homogeneous electron gas → lCCD and rCCD are divergent[6].
- This divergence can be eliminated by adding the mosaic terms.
- The mosaic terms self-consistently renormalise the one-electron energy[7].

$$F_i^l = \epsilon_i \delta_{il} + \frac{1}{2} \langle kl || cd \rangle \, t_{ik}^{cd} \tag{2}$$

$$F_d^a = \epsilon_a \delta_{ad} - \frac{1}{2} \langle kl || cd \rangle \, t_{kl}^{ac} \tag{3}$$

[6] James J. Shepherd, Thomas M. Henderson, and Gustavo E. Scuseria (2014a). "Coupled Cluster Channels in the Homogeneous Electron Gas". In: *J. Chem. Phys.* 140, p. 124102.

[7] James J. Shepherd, Thomas M. Henderson, and Gustavo E. Scuseria (2014b). "Range-Separated Brueckner Coupled Cluster Doubles Theory". In: *Phys. Rev. Lett.* 112, p. 133002.