Many-body Perturbation Theory formulated in terms of physically motivated parameters for 1D atomic chains

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Contributions to the correlation energy at MP2 level are examined for a finite chain of hydrogen atoms. We demonstrate that restricting oneself to a subset of MP2 terms, such as pair-states, either doesn't involve a scaling reduction or vanishes at the thermodynamic limit†. Similarities between the terms do appear, and allow for them to be classified by three effective parameters, i.e. momentum transfer, depth and asymmetry of the corresponding diagram. Formulating the perturbative series with respect to these physically motivated parameters not only gives an insight regarding the magnitude of terms, but also allows for their separation into similar groups. Integrating over such groups leads to a size extensive scheme, with bounds on error, that does involve a scaling reduction. As a proof of concept the method was benchmarked against full MP2 and CCSD with STO-6G and cc-pVDZ.

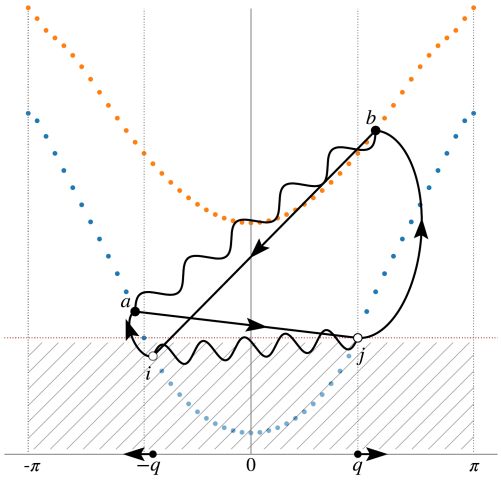

Figure 1: Exchange diagram of a two band H_{50} chain at quarter filling. Conservation of momenta restricts the momentum transfers $\mathbf{q}_{i\to a}$ and $\mathbf{q}_{j\to b}$ to be of same magnitude and opposite direction. Number of diagrams with given $\mathbf{q}$ is porportional to $\mathbf{q}^2$ and the magnitude is observed to sharply decay with increasing $\mathbf{q}$. Implications associated to dimensionality, the multi-band nature, and the role of the other two effective parameters are discussed.

[1] S. Kedžuch, J. Šimunek, M. Veis, J. Noga, J. Chem. Theory Comput., **16** (2020), 7372-7380.

[2] M. Veis, PhD. Thesis, Perturbative and coupled cluster methods utilizing the concept of electronic pair states, and the study of electronic, Comenius University Bratislava 2023.

†: This statement remains valid, for 1D chains at half-filling, regardless of the choice of the subset. Note that the scaling reduction associated with the translational symmetry is already acounted for.