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Reformulation of intermolecular perturbation theory using imaginary time

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It is shown that perturbation theory for interacting molecules within the framework of the interaction picture in quantum mechanics can be reformulated through integrals over products of imaginary time cross correlation functions, providing a natural way for its factorization. Thus in second order an alternative expression for the London dispersion energy contribution is obtained in which the standard Casimir-Polder integration over products of susceptibilities at imaginary frequencies is replaced with integration over products of cross correlation functions at imaginary frequencies [1]. Thanks to a relation of the latter to the Green's function of the unperturbed Hamiltonian in principle they are accessible through, e.g., Green's function or diffusion quantum Monte Carlo, numerical split operator imaginary time propagation, or other numerical and analytical path integral methods. In some cases like that of the harmonic oscillator they could even be determined analytically. Furthermore, susceptibilities and cross correlation functions can be related through a Fourier cosine transform. Besides a derivation and a discussion of the revamped second-order contributions extensions of the imaginary time approach to higher orders of perturbation theory will be presented.

[1] G. Jansen, "Factorization of static perturbation theory for weakly coupled systems using imaginary time", Phys. Rev. A 113, L030201 (2026).