

Two-particle properties from one-particle Green's functions: interpretation of electronic structure and application to single-molecule magnets

Pavel Pokhilko¹, Dominika Zgid^{1,2}

¹Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109, USA

²Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA

Properties of molecules and solids can be computed using Green's functions. However, these methods are not very well understood since the conventional analysis of electronic structure in terms of wave functions is not available. Moreover, only one-particle properties and certain thermodynamic observables (energy, grand potential) can be directly accessed through one-particle Green's function. We show that within self-consistent Green's function methods, the properties can be evaluated through the thermodynamic Hellmann–Feynman theorem. This theorem is valid for any time-dependent or time-independent observables, including two-particle observables. The two-particle density matrix, found from the first derivative of the grand potential, decomposes into an antisymmetrized direct product of one-electron correlated density matrices (disconnected term) and the electronic cumulant (connected part). The structure of the cumulant is produced by the vertex function, which is established from the self-energy functional. The traces of the two-particle density matrix obtained this way with two-electron integrals reproduce energy from Galitskii–Migdal formula following from the equation of motion of the field operators. This procedure avoids the solution of the computationally expensive Bethe–Salpeter equation. The explicit cumulant expressions for self-consistent GF2 and GW methods show the degree of violation of ensemble representability (generalization of N-representability to ensembles) of these methods. The obtained two-particle density matrices can rationalize the results of calculations through two-particle properties, such as $\langle S^2 \rangle$ and $\langle N^2 \rangle$, and establish deeper connections with the wave-function theories. Similarly to MP2 and CC2, GF2 and GW one- and two-particle density matrices do not have consistent perturbative orders with respect to the bare interaction and bold propagator, which leads to contamination of $\langle S^2 \rangle$ and $\langle N^2 \rangle$ at zero temperature. Two-particle local spin and charge statistical cumulants characterize the obtained solutions, quantifying their covalent and ionic degree. Spin cumulants also rationalize the broken-symmetry nature of solutions obtained for open-shell systems. Following E. Davidson and A. Clark, we use the spin cumulants to derive the effective spin Hamiltonians from the broken-spin solutions (Noodleman's approach). Applied to single-molecule magnets, we show that spin and charge cumulants can be used as a diagnostic of validity of Heisenberg Hamiltonian. In particular, a non-zero charge cumulant between iron centers in $\text{Fe}_2\text{OCl}_6^{2-}$ complex leads to a deviation from a Heisenberg picture through effective biquadratic spin interaction. The found effective exchange constant values are in agreement with the wave-function methods (EOM-SF-CCSD, CASSCF, and MRCI).