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Luis Lain, Alicia Torre, and Roberto Bochicchio

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NOTES

On the definition of the spin-free cumulant of the second-order reduced density matrix

Luis Lain[a)] and Alicia Torre
Department Química Física, Facultad de Ciencias. Universidad del País Vasco. Apdo. 644, E-48080 Bilbao, Spain

Roberto Bochicchio
Department Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria 1428, Buenos Aires, Argentina

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In a recent series of papers[1–4] Kutzelnigg and Mukherjee have described the cumulants of the reduced density matrices as well as their interesting properties in many-body theory. These authors have also set out the problem of defining the spin-free version of the cumulant of the second-order reduced density matrix.[4] The aim of this note is to reinforce one of the proposals given by these authors through a different approach involving the cumulant of the expectation value of the products of creation and annihilation operators, which leads to a more compact formulation.

According to previous works[1–4] we will adopt the following notation: Ψ is the state of an N-electron system, $\sigma_1,\ \sigma_2=\alpha,\ \beta$ are spin coordinates, P,Q,R,S are orbitals, $P\sigma_1,\ Q\sigma_2,\ldots$ are spin orbitals, $a^\dagger_{P\sigma}$ and $a_{R\sigma}$ are standard creation and annihilation fermion operators, $E^P_R=\Sigma_\sigma a^\dagger_{P\sigma}a_{R\sigma}$ are spin-free first-order replacement operators, $E^{PQ}_{RS}=\Sigma_{\sigma_1,\sigma_2}a^\dagger_{P\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}a_{R\sigma_1}$ are spin-free second-order replacement operators, $\gamma^{P\sigma}_{R\sigma}=\langle\Psi|a^\dagger_{P\sigma}a_{R\sigma}|\Psi\rangle$ are first-order reduced density matrix elements, $\eta^{Q\sigma}_{S\sigma}=\langle\Psi|a_{S\sigma}a^\dagger_{Q\sigma}|\Psi\rangle$ are first-order hole reduced density matrix elements, $\gamma^{P\sigma_1Q\sigma_2}_{R\sigma_1S\sigma_2}=\langle\Psi|a^\dagger_{P\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}a_{R\sigma_1}|\Psi\rangle$ are second-order reduced density matrix elements, $\Gamma^P_R=\langle\Psi|E^P_R|\Psi\rangle$ are spin-free first-order reduced density matrix elements, $H^Q_S=\langle\Psi|\Sigma_\sigma a_{S\sigma}a^\dagger_{Q\sigma}|\Psi\rangle$ are spin-free first-order hole reduced density matrix elements, $\Gamma^{PQ}_{RS}=\langle\Psi|E^{PQ}_{RS}|\Psi\rangle$ are spin-free second-order reduced density matrix elements, $\lambda^{P\sigma_1Q\sigma_2}_{R\sigma_1S\sigma_2}$ is the cumulant of the second-order reduced density matrix elements, and Λ^{PQ}_{RS} is the cumulant of the spin-free second-order reduced density matrix elements.

Using the well-known anticommutation rules of fermion operators, the second-order reduced density matrix elements can be expressed as

$$\gamma^{P\sigma_1Q\sigma_2}_{R\sigma_1S\sigma_2}=\langle\Psi|a^\dagger_{P\sigma_1}a_{R\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle-\langle\Psi|a^\dagger_{P\sigma_1}a_{S\sigma_2}|\Psi\rangle\,\delta_{Q\sigma_2R\sigma_1}. \tag{1}$$

The first term of the right-hand side (rhs) of this equation can be evaluated through the cumulant, or covariance, of the expectation value of the product of operators[5] $(a^\dagger_{P\sigma_1}a_{R\sigma_1})(a^\dagger_{Q\sigma_2}a_{S\sigma_2})$, which will be denoted as $\langle\Psi|a^\dagger_{P\sigma_1}a_{R\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle^c$:

$$\langle\Psi|a^\dagger_{P\sigma_1}a_{R\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle=\langle\Psi|a^\dagger_{P\sigma_1}a_{R_{\sigma_1}}|\Psi\rangle\langle\Psi|a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle+\langle\Psi|a^\dagger_{P\sigma_1}a_{R\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle^c. \tag{2}$$

The substitution of this expression in Eq. (1) as well as the formulation of the Kronecker delta $\delta_{Q\sigma_2R\sigma_1}=\gamma^{Q\sigma_2}_{R\sigma_1}+\eta^{Q\sigma_2}_{R\sigma_1}$ leads to

$$\gamma^{P\sigma_1Q\sigma_2}_{R\sigma_1S\sigma_2}=\gamma^{P\sigma_1}_{R\sigma_1}\gamma^{Q\sigma_2}_{S\sigma_2}-\gamma^{P\sigma_1}_{S\sigma_2}\gamma^{Q\sigma_2}_{R\sigma_1}-\gamma^{P\sigma_1}_{S\sigma_2}\eta^{Q\sigma_2}_{R\sigma_1}+\langle\Psi|a^\dagger_{P\sigma_1}a_{R\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle^c, \tag{3}$$

in which

$$\lambda^{P\sigma_1Q\sigma_2}_{R\sigma_1S\sigma_2}=-\gamma^{P\sigma_1}_{S\sigma_2}\eta^{Q\sigma_2}_{R\sigma_1}+\langle\Psi|a^\dagger_{P\sigma_1}a_{R\sigma_1}a^\dagger_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle^c \tag{4}$$

turns out to be equivalent to the cumulant of the second-order reduced density matrix reported by Kutzelnigg and Mukherjee.[3]

It is not trivial to express the corresponding spin-free concept Λ^{PQ}_{RS} by a simple sum $\Sigma_{\sigma_1,\sigma_2}\lambda^{P\sigma_1Q\sigma_2}_{R\sigma_1S\sigma_2}$ because the term $\Sigma_{\sigma_1,\sigma_2}\gamma^{P\sigma_1}_{S\sigma_2}\eta^{Q\sigma_2}_{R\sigma_1}$ is not independent of the spin coordinates. However, the sum in the spin coordinates of Eq. (3) leads to

$$\sum_{\sigma_1,\sigma_2}\gamma^{P\sigma_1 Q\sigma_2}_{R\sigma_1 S\sigma_2}=\sum_{\sigma_1,\sigma_2}\gamma^{P\sigma_1}_{R\sigma_1}\gamma^{Q\sigma_2}_{S\sigma_2} -\sum_{\sigma_1,\sigma_2}\left[\gamma^{P\sigma_1}_{S\sigma_2}\gamma^{Q\sigma_2}_{R\sigma_1}+\gamma^{P\sigma_1}_{S\sigma_2}\eta^{Q\sigma_2}_{R\sigma_1}\right] +\sum_{\sigma_1,\sigma_2}\langle\Psi|a^{\dagger}_{P\sigma_1}a_{R\sigma_1}a^{\dagger}_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle^{c} \quad (5)$$

in which the sum $\Sigma_{\sigma_1,\sigma_2}[\gamma^{P\sigma_1}_{S\sigma_2}\gamma^{Q\sigma_2}_{R\sigma_1}+\gamma^{P\sigma_1}_{S\sigma_2}\eta^{Q\sigma_2}_{R\sigma_1}]$ turns out to be a spin-free quantity that can be expressed in terms of the spin-free counterpart concepts and $\Sigma_{\sigma_1,\sigma_2}\langle\Psi|a^{\dagger}_{P\sigma_1}a_{R\sigma_1}a^{\dagger}_{Q\sigma_2}a_{S\sigma_2}|\Psi\rangle^{c}$ is identical to $\langle\Psi|E^P_R E^Q_S|\Psi\rangle^c$. Hence, Eq. (5) can be written as

$$\Gamma^{PQ}_{RS}=\Gamma^P_R\Gamma^Q_S-\tfrac{1}{2}[\Gamma^P_S\Gamma^Q_R+\Gamma^P_S H^Q_R]+\langle\Psi|E^P_R E^Q_S|\Psi\rangle^c. \quad (6)$$

Consequently, from this equation the spin-free cumulant of the second-order reduced density matrix is

$$\Lambda^{PQ}_{RS}=-\tfrac{1}{2}\Gamma^P_S H^Q_R+\langle\Psi|E^P_R E^Q_S|\Psi\rangle^c, \quad (7)$$

which supports the definition which relates the spin-free second-order reduced density matrix and its corresponding cumulant matrix as[4]

$$\Gamma^{PQ}_{RS}=\Gamma^P_R\Gamma^Q_S-\tfrac{1}{2}\Gamma^P_S\Gamma^Q_R+\Lambda^{PQ}_{RS}. \quad (8)$$

This expression constitutes one of the proposals of Kutzelnigg and Mukherjee for the definition of the spin-free second-order reduced density matrix cumulant. We have also used successfully this definition in relation with the study[6] of the matrix of effectively unpaired electrons within statistical population analyses. In conclusion, the cumulants of the expectation values of products of fermion operators provide a compact formulation in the study of the partitionings of the elements of second-order reduced density matrices, as in the spin-free case as when spin coordinates are explicitly used.

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[a]Author to whom correspondence should be addressed. Electronic address: qfplapel@lg.ehu.es

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