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Some Comments About Trivial Hypervirial Relationships

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Trivial and non-trivial conditions under which off-diagonal hypervirial theorems are satisfied are discussed.

Key words: Off-diagonal hypervirial theorems.

The hypervirial relationships (HR) in the diagonal form (DHR)

$$(A, (HW - WH)A) = 0 \tag{1}$$

as well as in the off-diagonal form (ODHR)

$$(A, (HW - WH)B) = (E_B - E_A)\,(A, WB) \tag{2}$$

have been employed at a large extent to approximate the solutions of the Schrödinger equation. Several authors [1–3] have called attention to the DHR which are trivially satisfied due to different reasons. For example, let us suppose that A is a well behaved function and H_A is a pseudo-Hamiltonian operator built upon such a function, i.e.

$$H_A = T + V_A; \qquad V_A = e_A - \frac{TA}{A}. \tag{3}$$

Then, if W is a coordinate-dependent operator and assuming that the potential energy is only coordinate dependent too, the DHR

$$(A, (HW - WH)A) = (A, (H_A W - WH_A)A) = 0 \tag{4}$$

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is trivially satisfied, and consequently there is no interest regarding the optimization of A. This result was reported by Katriel and Adam [4] for a particular case through a somewhat different argument.

In this communication we wish to show that in certain cases the ODHR, which are trivially satisfied, have been applied in the past without being aware of this fact. Let us assume that B is an approximate function by means of which it is desired to optimize another trial function A utilizing the ODHR. If the hypervirial operator W commutes with V, then Eq. (2) turns to

$$(A, (HW - WH)B) = (A, (TW - WT)B) = (E_A - E_B)(A, WB). \tag{5}$$

Owing to the fact that relationship (5) does not contain the potential term, it is independent of the physical model, and therefore it has no value for optimizing A. From Eq. (3) we can re-write Eq. (5) as

$$(A, (H_B W - WH_B)B) = (E_A - E_B)(A, WB). \tag{6}$$

Obviously, at the most, we can get that A is an eigenfunction of H_B. Then, A will be a better function when H_B is more alike to H. These remarks allow us to point out some important details about previous works on hypervirials:

(a) When B is eigenfunction of H [4–7], $H_B = H$ and ODHR are not trivial.
(b) When A and B are approximate functions and only ODHR are used [8], the results have no meaning from a formal point of view, because H_B depends on the chosen function B.
(c) If ODHR are combined with the virial theorem or with another DHR which allow to optimize B [9, 10], the results have some significance because the employed relationships applied to determine B are not independent of the potential function V.

References

1. Katriel, J., Adam, G.: J. Phys. **B5**, 1 (1972)
2. Epstein, S. T.: J. Phys. **B7**, L431 (1974)
3. Fernández, F. M., Castro, E. A.: Theoret. Chim. Acta (Berl.) **59**, 87 (1981)
4. Bradley, C. J., Hughes, D. E.: Int. J. Quantum Chem. **3**, 699 (1969)
5. Castro, E. A.: Int. J. Quantum Chem. **14**, 231 (1978)
6. Castro, E. A.: Anal. Soc. Cient. Argentina **CCVI**, 45 (1980)
7. Fernández, F. M., Castro, E. A.: Int. J. Quantum Chem. **17**, 609 (1980)
8. Coulson, C. A., Nash, J. C.: J. Phys. **B7**, 657 (1974)
9. Gopinathan, M. S.: Int. J. Quantum Chem. **10**, 975 (1976)
10. Sakamoto, K., Terasaka, T.: Int. J. Quantum Chem. **16**, 1357 (1979)

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