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Balance in Forces Acting on Electrons in Molecules

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Synopsis. The force theorem is generalized by using the spin-specified momentum operator in the hypervirial theorem. A theorem consequent on this concerns a balance in forces acting on up- and down- spin electrons. The theorem is expected to be useful for examining accuracy of approximate wave functions for open-shell molecules.

In the previous paper[1)] the author has shown the spin virial theorem as a consequence of a generalization of the virial theorem, suggesting a natural way of deriving various spin-related theorems from the hypervirial theorem.[2)] Amongst such theorems, fundamental and significant in molecular electronic structure theory is a theorem obtained through a generalization of the force theorem.[3,4)] The theorem has lucid physical meaning, describing a balance in forces acting on up- and down-spin electrons.[5)] Although the derivation is rather straightforward, the explicit expression will be worth communicating with some remarks.

Let $\psi_\sigma(\boldsymbol{r})$ be the σ-spin component of the electron field operator. The spin index σ is allowed to take $\uparrow$ (up) or $\downarrow$ (down), $\boldsymbol{r}$ stading for spatial coordinates. We use the notation $\bar{\sigma}$ for the spin state opposite to σ in what follows. Suppose the electronic Hamiltonian consisting of the kinetic energy of electrons, the nuclear attraction potential, and the electronic repulsion potential. It is suitable for our purpose to retain the spin index; we put

$$H = \sum_\sigma (T_\sigma + V_\sigma + W_{\sigma\sigma} + W_{\sigma\bar{\sigma}}) \tag{1}$$

with

$$T_\sigma = \int \psi_\sigma^\dagger(\boldsymbol{r})(-\nabla^2/2)\psi_\sigma(\boldsymbol{r})\mathrm{d}\boldsymbol{r}, \tag{2}$$

$$V_\sigma = \int \psi_\sigma^\dagger(\boldsymbol{r}) \sum_\alpha (-Z_\alpha|\boldsymbol{r}-\boldsymbol{R}_\alpha|^{-1})\psi_\sigma(\boldsymbol{r})\mathrm{d}\boldsymbol{r}, \tag{3}$$

and

$$W_{\sigma\tau} = \frac{1}{2}\iint \psi_\sigma^\dagger(\boldsymbol{r})\psi_\tau^\dagger(\boldsymbol{q})|\boldsymbol{r}-\boldsymbol{q}|^{-1}\psi_\tau(\boldsymbol{q})\psi_\sigma(\boldsymbol{r})\mathrm{d}\boldsymbol{q}\mathrm{d}\boldsymbol{r}, \tag{4}$$

where Z_α and $\boldsymbol{R}_\alpha$ are the atomic number and the position of the α-th nucleus, respectively. Of course, we have

$$W_{\uparrow\downarrow} = W_{\downarrow\uparrow}. \tag{5}$$

On the other hand, we define the momentum operator as

$$\boldsymbol{P}_\sigma = \int \psi_\sigma^\dagger(\boldsymbol{r})(-\mathrm{i}\nabla)\psi_\sigma(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \quad (\sigma=\uparrow,\downarrow), \tag{6}$$

specifying the spin state. What is to be done is to work out the commutator between $\boldsymbol{P}_\sigma$ and H.

Among the commutators of $\boldsymbol{P}_\sigma$ with the constituents of H, only the two kinds are nonvanishing:

$$[V_\sigma, \boldsymbol{P}_\sigma] = -\mathrm{i}\boldsymbol{F}_\sigma \tag{7}$$

and

$$[W_{\sigma\bar{\sigma}}, \boldsymbol{P}_\sigma] = -\mathrm{i}\boldsymbol{B}_{\sigma\bar{\sigma}}/2, \tag{8}$$

where

$$\boldsymbol{F}_\sigma = \int \psi_\sigma^\dagger(\boldsymbol{r}) \sum_\alpha (-Z_\alpha(\boldsymbol{r}-\boldsymbol{R}_\alpha)|\boldsymbol{r}-\boldsymbol{R}_\alpha|^{-3})\psi_\sigma(\boldsymbol{r})\mathrm{d}\boldsymbol{r} \tag{9}$$

and

$$\boldsymbol{B}_{\sigma\bar{\sigma}} = \iint \psi_\sigma^\dagger(\boldsymbol{r})\psi_{\bar{\sigma}}^\dagger(\boldsymbol{q})(\boldsymbol{r}-\boldsymbol{q})|\boldsymbol{r}-\boldsymbol{q}|^{-3}\psi_{\bar{\sigma}}(\boldsymbol{q})\psi_\sigma(\boldsymbol{r})\mathrm{d}\boldsymbol{q}\mathrm{d}\boldsymbol{r}. \tag{10}$$

We can regard $\boldsymbol{F}_\sigma$ and $\boldsymbol{B}_{\sigma\bar{\sigma}}$ as representing the forces exerted on σ-spin electrons by nuclei and by $\bar{\sigma}$-spin electrons, respectively. After all, since H contains $W_{\sigma\bar{\sigma}}$ twice, we obtain

$$[H, \boldsymbol{P}_\sigma] = -\mathrm{i}(\boldsymbol{F}_\sigma + \boldsymbol{B}_{\sigma\bar{\sigma}}). \tag{11}$$

It should be noted that

$$\boldsymbol{B}_{\uparrow\downarrow} = -\boldsymbol{B}_{\downarrow\uparrow}. \tag{12}$$

We often abbreviate $\boldsymbol{B}_{\uparrow\downarrow}$ to $\boldsymbol{B}$ below, $\boldsymbol{B}_{\downarrow\uparrow}$ being identically equal to $-\boldsymbol{B}$.

The hypervirial theorem asserts that an arbitrary stationary state of a system of the Hamiltonian H fulfils

$$\langle [H, A] \rangle = 0 \tag{13}$$

for any operator A of the system, the bracket standing for the stationary state expectation value. Now we adopt $\boldsymbol{P}_\uparrow \pm \boldsymbol{P}_\downarrow$ as A. A new result, to which we will refer tentatively as the spin force theorem, immediately follows besides the force theorem;

$$\begin{cases} \langle \boldsymbol{F} \rangle = 0 & (14) \\ \langle \Delta\boldsymbol{F} \rangle + \langle \Delta\boldsymbol{B} \rangle = 0 & (15) \end{cases}$$

with

$$\boldsymbol{F} = \boldsymbol{F}_\uparrow + \boldsymbol{F}_\downarrow, \tag{16}$$

$$\Delta\boldsymbol{F} = \boldsymbol{F}_\uparrow - \boldsymbol{F}_\downarrow \tag{17}$$

and

$$\Delta\boldsymbol{B} = \boldsymbol{B}_{\uparrow\downarrow} - \boldsymbol{B}_{\downarrow\uparrow} = 2\boldsymbol{B}. \tag{18}$$

From now on, we abbreviate the force theorem to FT and the spin force theorem to SFT. Whereas FT is derivable also from the electrostatic theorem,[6)] SFT is not. The latter has no classical counterpart in a strict sense, being inherently quantum-mechanical. If $\boldsymbol{P}_\uparrow$ and $\boldsymbol{P}_\downarrow$ are taken as A, we have the set of equations tantamount to the set of FT and SFT;

$$\begin{cases} \langle \boldsymbol{F}_\uparrow \rangle + \langle \boldsymbol{B} \rangle = 0 & (19) \\ \langle \boldsymbol{F}_\downarrow \rangle - \langle \boldsymbol{B} \rangle = 0, & (20) \end{cases}$$

where FT is implicit. Here note that each of the above two equations is equivalent to SFT under FT because of

$$\langle \boldsymbol{\Delta F} \rangle = 2\langle \boldsymbol{F}_{\uparrow} \rangle = -2\langle \boldsymbol{F}_{\downarrow} \rangle. \tag{21}$$

An important point is that SFT directly concerns the interelectronic interaction in sharp contrast to FT.

The molecular symmetry sometimes makes FT trivial.[4] The same is true for SFT, the simplest example being atoms and homonuclear diatomic molecules. In particular, the symmetry in distributions of up- and down-spin electrons is enough for SFT (aside from FT). For most of molecular open-shell systems SFT is obviously meaningful. One can thus utilize SFT together with FT for examining accuracy of approximate wave functions for such systems. The fulfillment of these theorems is a necessary condition for sound approximate wave functions.[7] Surely it is interesting to see how far the theorems hold for elaborate approximate wave functions obtained with various advanced methods; this will be entrusted to computational chemists. Finally we add that SFT lets the spin virial theorem be origin-independent as FT does the virial theorem.[4]

References

1) M. Isihara, *Bull Chem. Soc. Jpn.*, **58**, 2472 (1985).

2) J. O. Hirschfelder, *J. Chem. Phys.*, **33**, 1462 (1960).

3) One should not confuse the force theorem with the Hellmann–Feynman theorem or the electrostatic theorem.

4) S. T. Epstein, "The Variation Method in Quantum Chemistry," Academic Press, New York (1974), Section 18.

5) Strictly speaking, we should say "electrons in the up-spin state" instead of "up-spin electrons" which is used throughout for convenience.

6) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939); A. C. Hurley, *Proc. R. Soc. London A*, **226**, 170 (1954).

7) The unrestricted Hartree-Fock function fulfills SFT as well as FT (in the exact limit of approximation). For this point, see Ref. 1.