Theoret. Chim. Acta (Berl.) 52, 89–91 (1979)

THEORETICA CHIMICA ACTA

Short Communication

Hypervirial Theorems and Symmetry

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It is pointed out that to ensure that an optimal variational wave function ψ having a certain symmetry satisfies the hypervirial theorem for W, it is sufficient that $iSW\psi$, where S is the projector onto the symmetry type in question, be a possible variation of ψ. Application is made to the tensor hypervirial theorem for atoms.

Key words: Hypervirial theorem – Symmetry

An optimal variational wave function satisfies

$$(\delta\psi, (H - E)\psi) + (\psi, (H - E)\delta\psi) = 0. \tag{1}$$

The usually invoked condition, which ensures that it also satisfies the hypervirial theorem [1]

$$(\psi, (HW - WH)\psi) = 0 \tag{2}$$

for a Hermitian operator W, is then that [2]

$$iW\psi \tag{3}$$

be a possible $\delta\psi$. It is the purpose of this note to draw attention to the fact that this condition may well be in conflict with the symmetry properties of ψ, and to replace it by another condition which does not have this defect.

More precisely, it can happen that $iW\psi$ does not have the symmetry of ψ and so for this reason alone, may not be a possible $\delta\psi$.[1] At one extreme, if $iW\psi$ itself has a definite symmetry, by hypothesis different from that of ψ, then this is no problem

[1] We say "may" because this depends on the nature of the set of trial functions.

0040-5744/79/0052/0089/$01.00

since (2) is then satisfied simply for reasons of symmetry.[2] However, as we will see by example below, it is not always the case that $iW\psi$ has a definite symmetry.

Thus we would like a sufficient condition which respects the symmetry of ψ, and indeed having stated the problem its solution is almost self-evident. Namely if S (which commutes with H) is the projector onto the symmetry type in question, then it is easy to show that it is also sufficient that

$$iSW\psi, \tag{4}$$

which does have the same symmetry as ψ, be a possible $\delta\psi$.

If S and W commute so that (4) has the same symmetry as ψ then, since $S\psi = \psi$, (4) is the same as (3). If at the other extreme, $iW\psi$ has a definite symmetry different from that of ψ, then since $SW\psi = 0$, we recover the result that in such cases no special considerations beyond symmetry are needed to ensure (2). To give an intermediate example, consider an N-electron system with $W = f(1)$, i.e. W depends only on the coordinates of electron 1. Then $iW\psi$ is not antisymmetric if ψ is, and hence would not usually be a possible $\delta\psi$. One then readily finds that (4), with S the antisymmetrizer, is proportional to

$$\left(i \sum_{s=1}^{N} f(s)\right)\psi \tag{5}$$

and hence we have derived the (obvious given that ψ is antisymmetric) result that the hypervirial theorem for $f(1)$ will be satisfied if that for $\sum_{s=1}^{N} f(s)$ is satisfied.

Our remaining examples are concerned with the tensor virial theorem [4, 5] for atoms. Here we deal with the set of operators

$$W_{ij} = \sum_{s=1}^{N} (p_i(s)x_j(s) + x_j(s)p_i(s)), \qquad i, j = x, y, z. \tag{6}$$

If we suppose that ψ is an eigenfunction of L_z, the z-component of angular momentum then one readily finds that symmetry alone ensures that the off-diagonal theorems are satisfied, and that the W_{xx} theorem will be satisfied if the W_{yy} theorem is. Thus if we have an eigenfunction of L_z then all theorems will be satisfied if the W_{zz} theorem and the ordinary virial theorem (the $W_{xx} + W_{yy} + W_{zz} \equiv V$ theorem) are satisfied.

Now to ensure that (3), with $W = V$, is a possible variation it is known [6] that one should allow for a uniform scaling of all electronic coordinates, while to ensure that (3) with $W = W_{zz}$ be a possible variation one should [4] also allow for an extrascaling of the z-coordinates. Further clearly neither of these scalings will upset the property of being an eigenfunction of L_z since the former leaves all angles unchanged while the latter leaves all azimuthal angles unchanged. However, the latter scaling obviously does conflict with having an eigenfunction of L^2, and so if one wants also to have an eigenfunction of L^2 one must turn to (4), with S the

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[2] Examples can be found on pages 96–101 of [3].

projector onto the eigenvalue of L^2, and with $W = W_{zz}$ in order to learn what to do. If one does this for a single electron in a central field

$$\psi = R(r)\, Y_{1m} \tag{7}$$

one readily finds that, to within an irrelevant additive multiple of ψ, $iSW_{zz}\psi$ is proportional to

$$r\,\frac{dR}{dr}\,Y_{lm}, \tag{8}$$

i.e. is proportional to $iV\psi$, and so one has the result that if the ordinary virial theorem is satisfied, then all the tensor theorems will be satisfied.

For the even parity $M = 0$ P-states[3] of helium [7]

$$\psi = (x_1y_2 - x_2y_1)F(r_1, r_2, \boldsymbol{r}_1\cdot\boldsymbol{r}_2) \tag{9}$$

one again finds after a bit of straight-forward "Clebsch-Gordanry" that $iSW_{zz}\psi$ is essentially the same as $iV\psi$, so again if the ordinary virial theorem is satisfied then the tensor theorems will also be satisfied.

Finally, we have looked at the odd parity $M = 0$ P-states of helium, but have not been able to complete the analysis. Here [7]

$$\psi = z_1F(r_1, r_2, \boldsymbol{r}_1\cdot\boldsymbol{r}_2) + z_2F(r_2, r_1, \boldsymbol{r}_1\cdot\boldsymbol{r}_2) \equiv z_1F + z_2\tilde{F} \tag{10}$$

and one finds that

$$3r_1\frac{\partial F}{\partial r_1} + r_2\frac{\partial F}{\partial r_2} + 4(\boldsymbol{r}_1\cdot\boldsymbol{r}_2)\frac{\partial F}{\partial \boldsymbol{r}_1\cdot\boldsymbol{r}_2} + 2\frac{(\boldsymbol{r}_1\cdot\boldsymbol{r}_2)}{r_1}\frac{\partial\tilde{F}}{\partial r_1} + r_2^2\frac{\partial\tilde{F}}{\partial(\boldsymbol{r}_1\cdot\boldsymbol{r}_2)} \tag{11}$$

should be a possible δF. The first three terms can be realized by a simple scaling (different for r_1 and r_2), however, we have thus far been unable to see how to implement the last two terms.[4]

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Received December 27, 1978

[3] Evidently for an atomic S-state, symmetry alone will ensure the tensor theorem if the ordinary theorem is satisfied.

[4] Equivalently we have not been able to evaluate $(\exp iaSW_{zz}S)\psi$ where a is a real constant. It is perhaps of interest to note, however, that if $F = F(r_1, r_2^2(1 - 2\cos^2\theta_n))$ then the second line vanishes identically.