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TIME-DEPENDENT HYPERVIRIAL THEOREMS AND THE LIKE

FOR VARIATIONAL WAVE FUNCTIONS

by

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ABSTRACT

Conditions are given under which optimal variational wave functions will satisfy time-dependent hypervirial theorems, Hellmann-Feynman theorems, etc.

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Let Φ_x and Φ_y be optimal time dependent variation wave functions appropriate to the Hamiltonians H_x and H_y respectively. Φ_x and Φ_y thus satisfy the variational equations[1]

$$(\delta \Phi_x, (H_x - i\hbar \frac{\partial}{\partial t}) \Phi_x) = 0 \tag{1a}$$

$$((H_x - i\hbar \frac{\partial}{\partial t}) \Phi_x, \delta \Phi_x) = 0 \tag{1b}$$

$$(\delta \Phi_y, (H_y - i\hbar \frac{\partial}{\partial t}) \Phi_y) = 0 \tag{2a}$$

$$((H_y - i\hbar \frac{\partial}{\partial t}) \Phi_y, \delta \Phi_y) = 0 \tag{2b}$$

Let us suppose that

$$\delta \Phi_x = \eta F \Phi_y \tag{3}$$

with η a small parameter, is a possible variation of Φ_x. From (1b) this then implies

$$((H_x - i\hbar \frac{\partial}{\partial t}) \Phi_x, F \Phi_y) = 0 \tag{4}$$

Similarly if

$$\delta \Phi_y = \eta F^{+} \Phi_x \tag{5}$$

with F^{+} the Hermitian conjugates of F , is a possible variation of Φ_y then (2a) implies

$$\left(F^{+} \Phi_x, \left(H_y - i\hbar \frac{\partial}{\partial t}\right) \Phi_y\right) = \left(\Phi_x, F\left(H_y - i\hbar \frac{\partial}{\partial t}\right) \Phi_y\right) = 0 \tag{6}$$

Subtracting (6) from (4) and using the Hermitian property of H_x we then have

$$\left(\Phi_x, (H_x F - F H_y) \Phi_y\right) + i\hbar \left(\frac{\partial \Phi_x}{\partial t}, F \Phi_y\right) + i\hbar \left(\Phi_x, F \frac{\partial \Phi_y}{\partial t}\right) = 0$$

or

$$\left(\Phi_x, (H_x F - F H_y) \Phi_y\right) + i\hbar \frac{d}{dt} \left(\Phi_x, F \Phi_y\right) - i\hbar \left(\Phi_x, \frac{\partial F}{\partial t} \Phi_y\right) = 0$$

or finally

$$\frac{d}{dt} \left(\Phi_x, F \Phi_y\right) = \left(\Phi_x, \frac{\partial F}{\partial t} \Phi_y\right) + \frac{i}{\hbar} \left(\Phi_x, (H_x F - F H_y) \Phi_y\right) \tag{7}$$

For $H_x \equiv H_y$ (7) might well be called a time-dependent (off-diagonal if $\Phi_x \neq \Phi_y$) hypervirial theorem while for $F = 1$, (7) becomes the time-dependent integral Hellmann-Feynman theorem of Hayes and Parr[2], though now for optimal variational functions.

Now let us suppose that

$$\delta \Phi_x = \eta \frac{\partial \Phi_x}{\partial \lambda} \tag{8}$$

with λ a real parameter, is a possible variation of Φ_x. Then from (1a) we have

$$\left(\frac{\partial \Phi_x}{\partial \lambda}, \left(H_x - i\hbar \frac{\partial}{\partial t}\right) \Phi_x \right) = 0 \tag{9}$$

while from (1b) we have

$$\left(\left(H_x - i\hbar \frac{\partial}{\partial t}\right) \Phi_x, \frac{\partial \Phi_x}{\partial \lambda} \right) = 0 \tag{10}$$

Also let us suppose that

$$\delta \Phi_x = \eta \Phi_x$$

is a possible variation of Φ_x so that from (1a) we have

$$\left(\Phi_x, \left(H - i\hbar \frac{\partial}{\partial t}\right) \Phi_x \right) = 0 \tag{11}$$

Consider now

$$\frac{\partial}{\partial\lambda}(\Phi_x, H_x\Phi_x) = \left(\Phi_x, \frac{\partial H_x}{\partial\lambda}\Phi_x\right) + \left(\frac{\partial\Phi_x}{\partial\lambda}, H_x\Phi_x\right) + \left(\Phi_x, H_x\frac{\partial\Phi_x}{\partial\lambda}\right) \quad (12)$$

Using (9) and (10) one readily finds that the last two terms on the right hand side can be written as

$$i\hbar\left(\frac{\partial\Phi_x}{\partial\lambda}, \frac{\partial\Phi_x}{\partial t}\right) - i\hbar\left(\frac{\partial\Phi_x}{\partial t}, \frac{\partial\Phi_x}{\partial\lambda}\right)$$

while from (11), the left hand side of (12) can be written as

$$i\hbar\frac{\partial}{\partial\lambda}\left(\Phi_x, \frac{\partial\Phi_x}{\partial t}\right) = i\hbar\left(\frac{\partial\Phi_x}{\partial\lambda}, \frac{\partial\Phi_x}{\partial t}\right) + i\hbar\left(\Phi_x, \frac{\partial^2\Phi_x}{\partial t\partial\lambda}\right)$$

Putting all this together then, (12) can be written

$$i\hbar\left(\Phi_x, \frac{\partial^2\Phi_x}{\partial t\partial\lambda}\right) + i\hbar\left(\frac{\partial\Phi_x}{\partial t}, \frac{\partial\Phi_x}{\partial\lambda}\right) = \left(\Phi_x, \frac{\partial H_x}{\partial\lambda}\Phi_x\right)$$

or

$$i\hbar\frac{\partial}{\partial t}\left(\Phi_x, \frac{\partial\Phi_x}{\partial\lambda}\right) = \left(\Phi_x, \frac{\partial H_x}{\partial\lambda}\Phi_x\right) \quad (13)$$

which is the time-dependent differential Hellmann-Feynman theorem of Hayes and Parr[2], though now for optimal variational functions.

Footnotes and References

1. J. Frenkel, Wave Mechanics, Advanced General Theory (Clarendon Press, Oxford, England, 1934) p. 436.
2. E. F. Hayes and R. G. Parr, J. Chem. Phys., 43, 1831 (1965). They also derive equation (7) for exact wave functions.