Tensor Virial Theorems for Variational Wave Functions

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It is shown that the tensor virial theorem and certain generalizations of it are satisfied by optimum energy variational wave functions in which the variational parameters are elements of a square matrix that scales the column matrix of particle coordinates.

I. INTRODUCTION

It has been shown by Epstein and Hirschfelder[1] that a sufficient condition for an optimum energy variational wave function Ψ_0 to satisfy the hypervirial theorem

$$(\Psi_0,[W,H]\Psi_0)=0 \tag{1}$$

is for the trial function Ψ to admit variations of the form $\partial\Psi/\partial\alpha=i/\hbar W\Psi$, where H is the Hamiltonian operator, W is an Hermitian operator, α is a variational parameter, $[W,H]\equiv WH-HW$ is the commutator of W and H, and $(\Psi,\Phi)=\int\Psi^*\Phi d\tau$ is the overlap integral between the two functions Ψ and Φ. The energy E, of course, is defined by the relation

$$E(\Psi,\Psi)=(\Psi,H\Psi). \tag{2}$$

Fock[2] showed that if a parameter is introduced into an approximate wave function in such a way that all distances are scaled, and if the parameter is varied so as to obtain the optimum energy, then the corresponding optimum function satisfies the familiar virial theorem to which Eq. (1) reduces[3] for $W=\frac{1}{2}(x_{\rho j}p_{\rho j}+p_{\rho j}x_{\rho j})$. Here, and henceforth, $x_{\rho j}$ is the jth Cartesian coordinate for the ρth particle of an N-particle system, and we use the summation convention that repeated Greek subscripts are summed from 1 to N while repeated Italic subscripts are summed from 1 to 3. Fock's original proof requires that the potential for the system be a homogeneous function of the coordinates, but Epstein and Hirschfelder have given a proof which does not depend upon the nature of the Hamiltonian. We shall give an alternative proof to that of Epstein and Hirschfelder and shall then give a generalization of Fock's result, showing that the tensor virial theorem[4] and certain generalized tensor virial theorems are satisfied by optimum energy variational wave functions in which the variational parameters are elements of a square matrix which scales the column matrix of particle coordinates. Epstein and Hirschfelder have given a *formal* variational function such that the optimal function satisfies the hypervirial theorems for several W's simultaneously. Our matrix scaling gives the explicit functional form of these formal functions for W's which correspond to tensor virial theorems.

[1] S. J. Epstein and J. O. Hirschfelder, Phys. Rev. **123**, 1495 (1961).
[2] V. Fock, Z. Physik **63**, 855 (1930).
[3] J. O. Hirschfelder, J. Chem. Phys. **33**, 1762 (1960).
[4] E. Parker, Phys. Rev. **96**, 1686 (1954).

II. SCALING AND THE VIRIAL THEOREM

If $\Psi=\Psi(y_{\rho j})$ where $y_{\rho j}=\Lambda x_{\rho j}$, then the coordinates $x_{\rho j}$ are said to be scaled by the parameter Λ. Notice that

$$\frac{\partial\Psi}{\partial\Lambda}=\frac{\partial\Psi}{\partial y_{\rho j}}\frac{\partial y_{\rho j}}{\partial\Lambda}=\frac{\partial\Psi}{\partial y_{\rho j}}x_{\rho j} \tag{3}$$

and similarly

$$\frac{\partial\Psi}{\partial x_{\rho j}}=\frac{\partial\Psi}{\partial y_{\sigma i}}\frac{\partial y_{\sigma i}}{\partial x_{\rho j}}=\frac{\partial\Psi}{\partial y_{\rho j}}\Lambda. \tag{4}$$

Upon using Eq. (4) to eliminate the quantity $\partial\Psi/\partial y_{\rho j}$ from Eq. (3), we obtain the identity

$$\Lambda\frac{\partial\Psi}{\partial\Lambda}=x_{\rho j}\frac{\partial\Psi}{\partial x_{\rho j}}. \tag{5}$$

Consider the result of optimizing E with respect to the (real) parameter Λ. Upon applying the operator $\Lambda\partial/\partial\Lambda$ to both sides of Eq. (2), differentiating under the integral sign, and then using Eq. (5), we obtain

$$\left(x_{\rho j}\frac{\partial\Psi}{\partial x_{\rho j}},H\Psi\right)+\left(\Psi,Hx_{\rho j}\frac{\partial\Psi}{\partial x_{\rho j}}\right)=\Lambda\frac{\partial E}{\partial\Lambda}(\Psi,\Psi)+E\left(x_{\rho j}\frac{\partial\Psi}{\partial x_{\rho j}},\Psi\right)+E\left(\Psi,x_{\rho j}\frac{\partial\Psi}{\partial x_{\rho j}}\right). \tag{6}$$

If we multiply Eq. (6) by $i\hbar$ and recognize that $(\hbar/i)\partial/\partial x_{\rho j}$ is just the momentum operator $p_{\rho j}$, we have

$$(x_{\rho j}p_{\rho j}\Psi,H\Psi)-(\Psi,Hx_{\rho j}p_{\rho j}\Psi)=i\hbar\Lambda\frac{\partial E}{\partial\Lambda}(\Psi,\Psi)+E(x_{\rho j}p_{\rho j}\Psi,\Psi)-E(\Psi,x_{\rho j}p_{\rho j}\Psi). \tag{7}$$

It follows from the fundamental commutation relations that $x_{\rho j}p_{\rho j}=W+i\hbar 3N/2$, where $W=\frac{1}{2}(x_{\rho j}p_{\rho j}+p_{\rho j}x_{\rho j})$. Upon substituting this expression for $x_{\rho j}p_{\rho j}$ into Eq. (7) and using Eq. (2) and the fact that W is Hermitian, we obtain the identity

$$i\hbar\Lambda\frac{\partial E}{\partial\Lambda}(\Psi,\Psi)=(\Psi,[W,H]\Psi). \tag{8}$$

It is clear from Eq. (8) that if Λ is varied so as to optimize E, then the corresponding optimum energy function Ψ_0 satisfies the virial theorem.

III. MATRIX SCALING AND TENSOR VIRIAL THEOREMS

If $\Psi=\Psi(y_{\rho j})$ where $y_{\rho j}=\Lambda_{jk}x_{\rho k}$, (same Λ_{jk} for all ρ), then we say that the column matrix of each particle's coordinates is scaled by the third-ordered square matrix $[\Lambda_{jk}]$. Notice that

$$\frac{\partial\Psi}{\partial\Lambda_{in}}=\frac{\partial\Psi}{\partial y_{\rho j}}\frac{\partial y_{\rho j}}{\partial\Lambda_{in}}=\frac{\partial\Psi}{\partial y_{\rho i}}x_{\rho n} \tag{9}$$

and similarly

$$\frac{\partial\Psi}{\partial x_{\rho m}}=\frac{\partial\Psi}{\partial y_{\sigma j}}\frac{\partial y_{\sigma j}}{\partial x_{\rho m}}=\frac{\partial\Psi}{\partial y_{\rho j}}\Lambda_{jm}. \tag{10}$$

Upon multiplying both sides of Eq. (10) by the element Λ_{mi}^{-1} of the inverse matrix to $[\Lambda_{mi}]$, we have

$$\frac{\partial\Psi}{\partial y_{\rho i}}=\frac{\partial\Psi}{\partial x_{\rho m}}\Lambda_{mi}^{-1}. \tag{11}$$

If we substitute this expression for $\partial\Psi/\partial y_{\rho i}$ into Eq. (9) and multiply the result by Λ_{ij}, we obtain the identity

$$\Lambda_{ij}\frac{\partial\Psi}{\partial\Lambda_{in}}=x_{\rho n}\frac{\partial\Psi}{\partial x_{\rho j}}. \tag{12}$$

An obvious generalization of the derivation given in Sec. II leads to the identity

$$i\hbar\Lambda_{ij}\frac{\partial E}{\partial\Lambda_{in}}(\Psi,\Psi)=(\Psi,[W_{nj},H]\Psi), \tag{13}$$

where $W_{nj}=\frac{1}{2}(x_{\rho n}p_{\rho j}+p_{\rho j}x_{\rho n})$. For this W, Eq. (1) reduces to the tensor virial theorem which has been discussed by Parker.[4] Hence, it is clear that if the nine elements of the matrix $[\Lambda_{in}]$ are varied independently so as to optimize E, then the corresponding optimum energy function Ψ_0 satisfies the nine relations of the tensor virial theorem.

IV. GENERALIZATIONS

It is easy to show that if $\Psi=\Psi(y_{\rho j})$ where $y_{\rho j}=\Lambda_{\rho j\sigma k}x_{\sigma k}$, and if each of the $9N^2$ elements of the matrix $[\Lambda_{\rho\sigma jk}]$ are varied independently so as to optimize E, then the corresponding optimum energy function Ψ_0 satisfies the hypervirial theorems for the $9N^2$ operators $W_{\rho\sigma jk}=\frac{1}{2}(x_{\rho j}p_{\sigma k}+p_{\sigma k}x_{\rho j})$.

However, for a system of identical particles, these operators are not observables, since they do not commute with the general permutation operator P. There are eighteen independent linear combinations of the $W_{\rho\sigma jk}$ that commute with P. Nine of these are just the W_{nj} of Eq. (13). The other nine are the operators $\bar{W}_{nj}=\frac{1}{2}\sum_{\rho\neq\sigma}W_{\rho\sigma nj}$. It is clear that the hypervirial theorems corresponding to $\bar{W}_{nj}$ express a correlation between the position of one particle and the momenta of another. It is not difficult to prove that if one sets $\Lambda_{\rho\sigma jk}$ equal to $\Lambda_{\alpha\beta jk}$ for $\rho\neq\sigma$ and $\alpha\neq\beta$, and sets $\Lambda_{\rho\rho jk}$ equal to $\Lambda_{\sigma\sigma jk}$ (no summation on ρ and σ), and if each of the eighteen independent elements of the matrix $[\Lambda_{\rho\sigma jk}]$ are varied so as to optimize E, then the corresponding optimum energy function Ψ_0 satisfies the hypervirial theorems for the eighteen operators W_{nj} and $\bar{W}_{nj}$.