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A New Theorem on an Internal Balance in the State Energy

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A theorem useful for checking the accuracy of the wave function is presented, which is especially valid and significant for open-shell systems. The theorem connects the kinetic and potential energies of electrons in the up- and down-spin states with one another through an antisymmetric quantity concerned with the spin polarization. Two mutually related derivations of the theorem are shown for the atomic system: One from the hypervirial theorem sets forth the general applicability and the other by the spin-dependent scaling clarifies the variational aspect. The numerical application to restricted and unrestricted analytic self-consistent field wave functions illustrates the sound nature of the theorem. Possibilities of its extension and generalization are touched upon briefly.

The state energy is undoubtedly a quantity of primary importance in the nonempirical calculation of electronic wave functions, not only because the quantity itself is the most fundamental that concerns many physical and chemical properties, but also because the approximate wave function is almost always calculated through the variation principle with the expectation value of the state energy as an indicator of accuracy. However, since the state energy given as an expectation value is of an extremely global character, the accuracy of the wave function cannot be checked enough if one concentrates exclusively on the lowering of the state energy expectation value.

It is, accordingly, quite reasonable to examine an expectation value of some physical quantity other than the state energy, provided that the "exact" value of the quantity is known. This way of checking may work effectively for specific problems under the appropriate choice of the quantity for examination, but it hardly seems to give any feeling for the general situation over various approximate wave functions of different systems.

One can also utilize relations between physical quantities which hold for the exact wave function or in the limit of a specific approximation. Although such relations can be often paraphrased into the form that the expectation value of a relevant composite quantity vanishes, there is qualitative difference between the use of a physical quantity with a known value and that of a physical relation, which is inherently nonempirical and commonly applicable. One of the most typical and important examples is the virial theorem[1–4] which has been frequently used in terms of the virial ratio check.

The virial ratio is, as a matter of course from its global character, not very sensitive in the high stage of approximation. It is true, however, that the virial theorem necessarily holds for the well-optimized wave function even without the gross scaling which forces the approximate wave function to satisfy the theorem. So is that the approximate wave function violating the theorem is more or less ill-behaved.

The usefulness of the virial theorem is mainly due to its intimate association with the state energy. Two dominant constituents of the state energy, the kinetic and potential energies, are subjected to a definite interrelation by the theorem, which is thus regarded as acquanting us with some detail of the state energy, an internal balance therein. Then, is there any other profitable theorem on another internal balance in the state energy?

In this paper we give an affirmative answer to this. The key observation is that a simple expression analogous with the virial relation is to be obtained separately for electrons in the up- and down-spin states. The expression is ready to lead us to a new theorem besides the virial theorem. The constituents participating in the new theorem are the kinetic and potential energies of electrons in the up- and down-spin states. They are connected with one another through an antisymmetric quantity concerned with the spin polarization. The theorem is, therefore, expected to be especially valid and significant in dealing with open-shell systems.

In the subsequent two sections, confining ourselves to the atomic system, we describe the derivation from the hypervirial theorem[5–8] and the derivation by the scaling dependent on the spin. The former is very transparent and clearly sets forth the applicability of the theorem, the latter clarifying the variational aspect. Next, a simple illustrative application is presented to restricted and unrestricted analytic self-consistent field (SCF) wave functions. After short concluding remarks, three appendices follow.

Derivation from the Hypervirial Theorem

Let $\{\phi_{j\sigma}(\boldsymbol{r})\xi_\sigma\}$ be a complete set of orthonormal spin orbitals, ξ_σ being the one-electron spin eigenfunction; σ stands for the one-electron spin state, taking $\uparrow$ (up) or $\downarrow$ (down), and $\boldsymbol{r}$ symbolizes the spatial coordinates with the origin at the atomic center. The notation $\bar{\sigma}$ is used to indicate the spin state opposite to σ in the following. Each of $\{\phi_{j\uparrow}(\boldsymbol{r})\}$ and $\{\phi_{j\downarrow}(\boldsymbol{r})\}$ are assumed to form a complete set of orthonormal spatial orbitals, though $\phi_{j\sigma}(\boldsymbol{r})$ is not necessarily identical with $\phi_{j\bar{\sigma}}(\boldsymbol{r})$.

Denoting the creation and annihilation operators for the spin orbital $\phi_{j\sigma}(\boldsymbol{r})\xi_\sigma$, respectively, by $a_{j\sigma}^\dagger$ and $a_{j\sigma}$, we can write the atomic electronic Hamiltonian in the second quantized form as

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

with

$$T_\sigma = \sum_{jk} t_{jk\sigma} a_{j\sigma}^\dagger a_{k\sigma}, \tag{2}$$

$$V_\sigma = \sum_{jk} v_{jk\sigma} a_{j\sigma}^\dagger a_{k\sigma}, \tag{3}$$

and

$$W_{\sigma\tau} = \frac{1}{2} \sum_{jklm} w_{lm\tau}^{jk\sigma} a_{j\sigma}^\dagger a_{l\tau}^\dagger a_{m\tau} a_{k\sigma}, \tag{4}$$

where

$$t_{jk\sigma} = \int \phi_{j\sigma}^*(\boldsymbol{r})(-\nabla^2/2)\phi_{k\sigma}(\boldsymbol{r})\mathrm{d}v, \tag{5}$$

$$v_{jk\sigma} = \int \phi_{j\sigma}^*(\boldsymbol{r})(-Z/r)\phi_{k\sigma}(\boldsymbol{r})\mathrm{d}v, \tag{6}$$

and

$$w_{lm\tau}^{jk\sigma} = \iint \phi_{j\sigma}^*(\boldsymbol{r}_1)\phi_{l\tau}^*(\boldsymbol{r}_2)(1/r_{12})\phi_{m\tau}(\boldsymbol{r}_2)\phi_{k\sigma}(\boldsymbol{r}_1)\mathrm{d}v_2\mathrm{d}v_1. \tag{7}$$

We abbreviate $|\boldsymbol{r}|$ to r and $|\boldsymbol{r}_1\text{-}\boldsymbol{r}_2|$ to r_{12} as usual; $\mathrm{d}v$ stands for the spatial volume element and Z for the atomic number. It holds that

$$W_{\sigma\tau} = W_{\tau\sigma} \tag{8}$$

as a direct consequence of $w_{lm\tau}^{jk\sigma} = w_{jk\sigma}^{lm\tau}$.

Now the hypervirial theorem asserts that an exact stationary state fulfils

$$\langle [H, F] \rangle = 0 \tag{9}$$

for arbitrary choice of an operator F of the system considered.[5-8)] The pure bracket means the expectation value in the exact stationary state. Introducing the virial operator for the spin state σ

$$G_\sigma = \sum_{jk} g_{jk\sigma} a_{j\sigma}^\dagger a_{k\sigma} \tag{10}$$

with

$$g_{jk\sigma} = -\frac{\mathrm{i}}{2}\int \phi_{j\sigma}^*(\boldsymbol{r})(\boldsymbol{r}\cdot\nabla + \nabla\cdot\boldsymbol{r})\phi_{k\sigma}(\boldsymbol{r})\mathrm{d}v, \tag{11}$$

we adopt this (or $G_\uparrow \pm G_\downarrow$) as F in the hypervirial theorem. Since $\nabla\cdot\boldsymbol{r}$ is converted into $\boldsymbol{r}\cdot\nabla$ plus a constant, the use of the non-hermitian virial operator containing only $\boldsymbol{r}\cdot\nabla$ is tantamount to that of the present operator under the Hamiltonian which conserves both the numbers of electrons in the up- and down-spin states. We prefer the hermitian form; it just fits the unitary transformation formalism. (See the next section and Appendix II.)

Because G_σ is commutative with $T_{\bar{\sigma}}$, $V_{\bar{\sigma}}$, and $W_{\bar{\sigma}\bar{\sigma}}$, we have only to calculate the commutators of G_σ with T_σ, V_σ, $W_{\sigma\sigma}$, and $W_{\sigma\bar{\sigma}}$. The one-electron commutators are readily found to be

$$[T_\sigma, G_\sigma] = -2\mathrm{i}T_\sigma \tag{12}$$

and

$$[V_\sigma, G_\sigma] = -\mathrm{i}V_\sigma. \tag{13}$$

For the two-electron commutators we have

$$[W_{\sigma\tau}, G_\sigma] = -\mathrm{i}(1+\delta_{\sigma\tau})(W_{\sigma\tau}+X_{\sigma\tau})/2 \tag{14}$$

with

$$X_{\sigma\tau} = \frac{1}{2}\sum_{jklm} x_{lm\tau}^{jk\sigma} a_{j\sigma}^\dagger a_{l\tau}^\dagger a_{m\tau} a_{k\sigma}, \tag{15}$$

where

$$x_{lm\tau}^{jk\sigma} = \iint \phi_{j\sigma}^*(\boldsymbol{r}_1)\phi_{l\tau}^*(\boldsymbol{r}_2)(1/\tilde{r}_{12})\phi_{m\tau}(\boldsymbol{r}_2)\phi_{k\sigma}(\boldsymbol{r}_1)\mathrm{d}v_2\mathrm{d}v_1 \tag{16}$$

with

$$\tilde{r}_{12} = r_{12}^3/(r_1^2 - r_2^2). \tag{17}$$

The property that $x_{lm\tau}^{jk\sigma} = -x_{jk\sigma}^{lm\tau}$ leads to

$$X_{\sigma\tau} = -X_{\tau\sigma} \tag{18}$$

in sharp contrast to $W_{\sigma\tau}$. Because of this antisymmetry it follows that

$$[W_{\sigma\sigma}, G_\sigma] = -\mathrm{i}W_{\sigma\sigma}, \tag{19}$$

but

$$[W_{\sigma\bar{\sigma}}, G_\sigma] = -\mathrm{i}(W_{\sigma\bar{\sigma}} + X_{\sigma\bar{\sigma}})/2. \tag{20}$$

The quantity $X_{\sigma\bar{\sigma}}$ is considered to represent the electronic repulsion potential "filtered" with the factor $(r_1^2 - r_2^2)/r_{12}^2$. It seems proper to refer to this quantity as the spin polarization potential. The point of calculation of the above commutators is given in Appendix I.

It is convenient to define the potential energy operator for the spin state σ as

$$U_\sigma = V_\sigma + W_{\sigma\sigma} + W_{\sigma\bar{\sigma}}. \tag{21}$$

The commutators in the preceding paragraph suffice to give

$$[H, G_\sigma] = -\mathrm{i}(2T_\sigma + U_\sigma + X_{\sigma\bar{\sigma}}), \tag{22}$$

which results in

$$2\langle T_\sigma \rangle + \langle U_\sigma \rangle + \langle X_{\sigma\bar{\sigma}} \rangle = 0 \quad (\sigma = \uparrow, \downarrow) \tag{23}$$

by virtue of the hypervirial theorem. By the relevant recombination in this set of equations, which is equivalent to using

$$\langle [H, G_\uparrow \pm G_\downarrow] \rangle = 0, \tag{24}$$

we obtain the virial theorem

$$2\langle T\rangle+\langle U\rangle = 0, \tag{25}$$

where

$$T = T_{\uparrow} + T_{\downarrow} \tag{26}$$

and

$$U = U_{\uparrow} + U_{\downarrow} = V_{\uparrow} + V_{\downarrow} + W_{\uparrow\uparrow} + W_{\downarrow\downarrow} + 2W_{\uparrow\downarrow}, \tag{27}$$

and the following theorem independent of the virial one.

$$2\langle \Delta T\rangle + \langle \Delta U\rangle + \langle \Delta X\rangle = 0 \tag{28}$$

with

$$\Delta T = T_{\uparrow} - T_{\downarrow}, \tag{29}$$

$$\Delta U = U_{\uparrow} - U_{\downarrow} = V_{\uparrow} - V_{\downarrow} + W_{\uparrow\uparrow} - W_{\downarrow\downarrow}, \tag{30}$$

and

$$\Delta X = X_{\uparrow\downarrow} - X_{\downarrow\uparrow} = 2X_{\uparrow\downarrow}. \tag{31}$$

We provisionally call this the spin virial theorem for the sake of convenience.

It is evident that the spin virial theorem as well as the virial theorem still holds even if the exact stationary state is replaced with any approximate state $|\Phi\rangle$that satisfies the one-electron hypervirial theorem[9)]

$$\langle \Phi|[H,\ a^{\dagger}_{j\sigma}a_{k\sigma}]|\Phi\rangle = 0 \quad (\text{any } j\sigma, k\sigma). \tag{32}$$

The most representative example is the unrestricted Hartree-Fock (HF) state and the restricted HF state for the closed-shell system. The restricted HF state for the open-shell system, however, does not satisfy the one-electron hypervirial theorem in general, even though it does

$$\langle \Phi|[H,\ a^{\dagger}_{j\uparrow}a_{k\uparrow}+a^{\dagger}_{j\downarrow}a_{k\downarrow}]|\Phi\rangle = 0 \quad (\text{any } j,\ k), \tag{33}$$

which is enough for the virial theorem to hold. The application to the approximate state with a specified form is thus often to be considered with respect to the exact limit of the approximation.

Scaling Dependent on the Spin

It is well known the close relation between the virial theorem and the positive gross scaling in the wave function, which can be worded in various manner.[4)] The essential point is still the equivalence of the virial theorem to the variational condition upon the scale factor incorporated into the wave function.[2)] The corresponding equivalence can be obtained also for the spin virial theorem. Here, in favor of naivety, we show a pedestrian approach starting with the explicit introduction of the spin-dependent scaling in orbitals, though the objective can be reached elegantly with the unitary transformation formalism,[6,8)] which is outlined in Appendix II for reference.

Now incorporating the spin-dependent scale factor into orbitals, we define the scaled orbitals as

$$\phi_{j\sigma}(\boldsymbol{r};\ \lambda_{\sigma}) = \lambda_{\sigma}^{3/2}\phi_{j\sigma}(\lambda_{\sigma}\boldsymbol{r}). \tag{34}$$

The orthonormality is preserved;

$$\int \phi^{*}_{j\sigma}(\boldsymbol{r};\ \lambda_{\sigma})\phi_{k\sigma}(\boldsymbol{r};\ \lambda_{\sigma})\mathrm{d}v=\delta_{jk}. \tag{35}$$

Soon it is seen to be suitable for our purpose to use the following parameters η and θ instead of $\lambda_{\uparrow}$ and $\lambda_{\downarrow}$.

$$\lambda_{\sigma} = \exp(\eta+\kappa_{\sigma}\theta) \tag{36}$$

with

$$\kappa_{\sigma} = \begin{cases} 1 & (\sigma=\uparrow) \\ -1 & (\sigma=\downarrow). \end{cases} \tag{37}$$

The creation and annihilation operators corresponding to the scaled spin orbital $\phi^{\eta\theta}_{j\sigma}(\boldsymbol{r})\xi_{\sigma}\equiv\phi_{j\sigma}(\boldsymbol{r};\lambda_{\sigma})\xi_{\sigma}$ are denoted by $a^{\eta\theta\dagger}_{j\sigma}$ and $a^{\eta\theta}_{j\sigma}$, respectively.

We can rewrite T_{σ}, V_{σ}, and $W_{\sigma\sigma}$ in the scaled representation simply as

$$T_{\sigma} = \exp(2(\eta+\kappa_{\sigma}\theta)) \sum_{jk} t_{jk\sigma}a^{\eta\theta\dagger}_{j\sigma}a^{\eta\theta}_{k\sigma}, \tag{38}$$

$$V_{\sigma} = \exp(\eta+\kappa_{\sigma}\theta) \sum_{jk} v_{jk\sigma}a^{\eta\theta\dagger}_{j\sigma}a^{\eta\theta}_{k\sigma}, \tag{39}$$

and

$$W_{\sigma\sigma} = \exp(\eta+\kappa_{\sigma}\theta)\frac{1}{2}\sum_{jklm} w^{jk\sigma}_{lm\sigma}a^{\eta\theta\dagger}_{j\sigma}a^{\eta\theta\dagger}_{l\sigma}a^{\eta\theta}_{m\sigma}a^{\eta\theta}_{k\sigma}, \tag{40}$$

whereas we have

$$W_{\sigma\bar{\sigma}} = \exp(\eta)\frac{1}{2}\sum_{jklm} w^{jk\sigma}_{lm\bar{\sigma}}(\theta)a^{\eta\theta\dagger}_{j\sigma}a^{\eta\theta\dagger}_{l\bar{\sigma}}a^{\eta\theta}_{m\bar{\sigma}}a^{\eta\theta}_{k\sigma}, \tag{41}$$

where

$$w^{jk\sigma}_{lm\bar{\sigma}}(\theta) = \iint \phi^{*}_{j\sigma}(\boldsymbol{r}_1)\phi^{*}_{l\bar{\sigma}}(\boldsymbol{r}_2)(1/r^{\sigma\bar{\sigma}}_{12}(\theta))\phi_{m\bar{\sigma}}(\boldsymbol{r}_2)\phi_{k\sigma}(\boldsymbol{r}_1)\mathrm{d}v_2\mathrm{d}v_1 \tag{42}$$

with

$$r^{\sigma\bar{\sigma}}_{12}(\theta) = |\exp(\kappa_{\bar{\sigma}}\theta)\boldsymbol{r}_1-\exp(\kappa_{\sigma}\theta)\boldsymbol{r}_2|. \tag{43}$$

As is implied by the notation, $w^{jk\sigma}_{lm\bar{\sigma}}(\theta)$ is independent of η, the η-dependence of the matrix element of $W_{\sigma\bar{\sigma}}$ being completely put into $\exp(\eta)$.

The expansion theorem[10)] allows us, without loss of generality, to write the exact or approximate state $|\mathrm{O}\rangle$ as

$$|\mathrm{O}\rangle = \sum_{M} C_M|M\rangle, \tag{44}$$

where C_{M} is a numerical coefficient and $|M\rangle$ is a single configuration state

$$|M\rangle = \prod_{j\sigma\in M} a^{\dagger}_{j\sigma}|\text{vacuum}\rangle \tag{45}$$

which is characterized by a set M of relevant spin orbital indices. The scaled state is obtained by replacing $a_{j\sigma}^{\eta\theta\dagger}$ with $a_{j\sigma}^{\dagger}$ in the original state;

$$|\eta\theta\rangle = \sum_{M} C_M |M\eta\theta\rangle \tag{46}$$

with

$$|M\eta\theta\rangle = \prod_{j^\sigma \in M} a_{j\sigma}^{\eta\theta\dagger}|\text{vacuum}\rangle. \tag{47}$$

The density matrices, $\gamma_{jk\sigma}$ and $\Gamma_{lm\tau}^{jk\sigma}$, are consequently kept unchanged;

$$\gamma_{jk\sigma} = \langle a_{j\sigma}^{\dagger} a_{k\sigma}\rangle_{\mathrm{O}} = \langle a_{j\sigma}^{\eta\theta\dagger} a_{k\sigma}^{\eta\theta}\rangle_{\eta\theta} \tag{48}$$

and

$$\Gamma_{lm\tau}^{jk\sigma} = \langle a_{j\sigma}^{\dagger} a_{l\tau}^{\dagger} a_{m\tau} a_{k\sigma}\rangle_{\mathrm{O}} = \langle a_{j\sigma}^{\eta\theta\dagger} a_{l\tau}^{\eta\theta\dagger} a_{m\tau}^{\eta\theta} a_{k\sigma}^{\eta\theta}\rangle_{\eta\theta}, \tag{49}$$

where $\langle\cdots\rangle_{\mathrm{O}}$ and $\langle\cdots\rangle_{\eta\theta}$ are short for the expectation value in $|\mathrm{O}\rangle$ and that in $|\eta\theta\rangle$. Thus it follows that

$$\langle T_\sigma\rangle_{\eta\theta} = \exp(2(\eta+\kappa_\sigma\theta))\langle T_\sigma\rangle_{\mathrm{O}}, \tag{50}$$

$$\langle V_\sigma + W_{\sigma\sigma}\rangle_{\eta\theta} = \exp(\eta+\kappa_\sigma\theta)\langle V_\sigma + W_{\sigma\sigma}\rangle_{\mathrm{O}}, \tag{51}$$

and

$$\langle W_{\sigma\bar\sigma}\rangle_{\eta\theta} = \exp(\eta)\frac{1}{2}\sum_{jklm} w_{lm\bar\sigma}^{jk\sigma}(\theta)\Gamma_{lm\bar\sigma}^{jk\sigma} \tag{52}$$

rather straightforwardly.

The differentiation of the above expectation values with respect to η and θ is trivial except that of $\langle W_{\sigma\bar\sigma}\rangle_{\eta\theta}$ with respect to θ. Going through

$$\frac{\partial}{\partial\theta} w_{lm\bar\sigma}^{jk\sigma}(\theta) = \kappa_\sigma x_{lm\bar\sigma}^{jk\sigma}(\theta), \tag{53}$$

where

$$x_{lm\bar\sigma}^{jk\sigma}(\theta) = \iint \phi_{j\sigma}^{*}(\boldsymbol{r}_1)\phi_{l\bar\sigma}^{*}(\boldsymbol{r}_2)(1/\tilde{r}_{12}^{\sigma\bar\sigma}(\theta))\phi_{m\bar\sigma}(\boldsymbol{r}_2)\phi_{k\sigma}(\boldsymbol{r}_1)\mathrm{d}v_2\mathrm{d}v_1 \tag{54}$$

with

$$\tilde{r}_{12}^{\sigma\bar\sigma}(\theta) = r_{12}^{\sigma\bar\sigma}(\theta)^3/(\exp(2\kappa_{\bar\sigma}\theta)r_1^2 - \exp(2\kappa_\sigma\theta)r_2^2), \tag{55}$$

we arrive at

$$\frac{\partial}{\partial\theta}\langle W_{\sigma\bar\sigma}\rangle_{\eta\theta} = \kappa_\sigma\langle X_{\sigma\bar\sigma}\rangle_{\eta\theta}, \tag{56}$$

since $\exp(\eta)x_{lm\bar\sigma}^{jk\sigma}(\theta)$ is just the matrix element of $X_{\sigma\bar\sigma}$ in the scaled representation;

$$X_{\sigma\bar\sigma} = \exp(\eta)\frac{1}{2}\sum_{jklm} x_{lm\bar\sigma}^{jk\sigma}(\theta) a_{j\sigma}^{\eta\theta\dagger} a_{l\bar\sigma}^{\eta\theta\dagger} a_{m\bar\sigma}^{\eta\theta} a_{k\sigma}^{\eta\theta}. \tag{57}$$

After all, we have

$$\frac{\partial}{\partial\eta}\langle T_\sigma\rangle_{\eta\theta} = 2\langle T_\sigma\rangle_{\eta\theta}, \tag{58}$$

$$\frac{\partial}{\partial\theta}\langle T_\sigma\rangle_{\eta\theta} = 2\kappa_\sigma\langle T_\sigma\rangle_{\eta\theta}, \tag{59}$$

$$\frac{\partial}{\partial\eta}\langle V_\sigma + W_{\sigma\sigma} + W_{\sigma\bar\sigma}\rangle_{\eta\theta} = \langle V_\sigma + W_{\sigma\sigma} + W_{\sigma\bar\sigma}\rangle_{\eta\theta}, \tag{60}$$

and

$$\frac{\partial}{\partial\theta}\langle V_\sigma + W_{\sigma\sigma} + W_{\sigma\bar\sigma}\rangle_{\eta\theta} = \kappa_\sigma(\langle V_\sigma + W_{\sigma\sigma}\rangle_{\eta\theta} + \langle X_{\sigma\bar\sigma}\rangle_{\eta\theta}). \tag{61}$$

Complete parallelism between the present treatment and the preceding one is quite clear in this step.

Using the above result with the notation defined before, we immediately obtain

$$\frac{\partial}{\partial\eta}\langle H\rangle_{\eta\theta} = 2\langle T\rangle_{\eta\theta} + \langle U\rangle_{\eta\theta} \tag{62}$$

and

$$\frac{\partial}{\partial\theta}\langle H\rangle_{\eta\theta} = 2\langle \varDelta T\rangle_{\eta\theta} + \langle \varDelta U\rangle_{\eta\theta} + \langle \varDelta X\rangle_{\eta\theta}, \tag{63}$$

which show that the variational condition

$$\frac{\partial}{\partial\eta}\langle H\rangle_{\eta\theta} = 0 \tag{64}$$

and

$$\frac{\partial}{\partial\theta}\langle H\rangle_{\eta\theta} = 0 \tag{65}$$

are equivalent to the virial theorem and the spin virial theorem. The exact wave function evidently lets these theorems hold. If θ is excluded out or fixed at zero throughout the treatment, the virial theorem results alone.[11)]

Now suppose that one has an approximate wave function violating both or either of the virial theorem and the spin virial theorem. The relevant scaling may be thought to improve the approximate wave function, making it satisfy the theorems; yet, aside from the case that the violation is conspicuous, the approximate wave function will not be improved genuinely with the sole use of the scaling. Here note that the completeness of a set of spin orbitals is assumed in the above, or else the Hamiltonian in the scaled representation inevitably differs from that in the original representation. Therefore, if one starts with an approximate wave function determined with some physical (presumably variational) condition in an incomplete space built of finite spin orbitals, then the scaled wave function may not fulfil the condition with respect to the "scaled" Hamiltonian.

Even in such a case, it is possible to invoke a practical iterative procedure: After the scaling process, calculate a wave function in the space built of the scaled spin orbitals with the predesignated condition, and go back to the scaling process with the calculated wave function as a new nonscaled wave function. This procedure is, however, not recommended as a general way of improving an approximate wave function in an incomplete space. The determination of η and θ is considerably laborious compared with that of the gross scale factor. It is rather important that the well-optimized, refined wave function is to fulfil the theorems without any scaling treatment. Here we only add that the spin-dependent scaling in a finite basis space necessarily leads us to "different bases for different spins,"[12] which does not match the spin restricted picture.

Illustrative Application

Here we apply the spin virial theorem to several restricted and unrestricted SCF wave functions obtained by the analytic expansion method,[13,14] using the spin virial ratio

$$\Omega_s = -(\overline{\Delta V}+\overline{\Delta W}+\overline{\Delta X})/(2\overline{\Delta T}), \tag{66}$$

where ΔV and ΔW are, respectively, the one- and two-electron components of ΔU. The upper bar means the expectation value for the wave function under consideration. Of course, the spin virial ratio takes unity if the theorem is satisfied. Our aim now is to realize the nature of the theorem rather than to test those wave functions.

For the present application, the above expectation values are reduced to the orbital integrals $t_{jj\sigma}$, $v_{jj\sigma}$, $w^{ij\sigma}_{kk\sigma}$, $w^{jk\sigma}_{kj\sigma}$, and $x^{ij\sigma}_{kk\sigma}$. Further, for the restricted case, we have only to take account of those integrals with which the singly occupied orbital is concerned. The integral of the spin polarization potential can be calculated analytically as well as the others. A few details of the integration are put in Appendix III.

The results are summarized in Tables 1—4. The state considered is ^{2}S for Li and Na, ^{2}P for B, and ^{4}S for N. The basis sets are from Clementi and Roetti's table,[15] unless otherwise specified. For the restricted case, we used the data of expansion coefficients in the published tables[15—17] directly with no SCF recalculation. Hence, the accuracy of the obtained values is a little degraded. The calculated values of the state energy

$$E = \overline{T} + \overline{U} \tag{67}$$

coincide with the published ones in five figures, and the virial ratio

$$\Omega_v = -\overline{U}/(2\overline{T}) \tag{68}$$

remains 1.0000 with the deviation about ±0.00001, being omitted in Tables 1 and 2. On the other hand, for the unrestricted case, we started with the SCF calculation using Clementi and Roetti's[15] and Weiss'[16] basis sets. Proper accuracy was sustained consistently.

Table 1 shows how the spin virial ratio varies with basis sets for the restricted case. The calculations for B, N, and Na exemplify the varying with the size of a basis set. We see a distinct gap between the single- and double-zeta results, the change being small beyond the double-zeta calculation. As the SCF wave function approaches the HF limit, the spin virial ratio appears to converge to the limit characteristic of the system. This is ascertained by the calculation for Li with different basis sets of fairly large size; the values of Ω_s are almost identical. As mentioned before, the open-shell HF wave function inherently violates the spin virial theorem,[18] so that the limit of convergence is not unity in general. Although the double-zeta results for B and N may look somewhat

TABLE 1. VARYING OF THE SPIN VIRIAL RATIO WITH BASIS SETS (*Restricted*)

System	Basis	$-E$/a.u.	Ω_s	$\overline{\Delta T}$/a.u.	$-\overline{\Delta V}$/a.u.	$\overline{\Delta W}$/a.u.	$\overline{\Delta X}$/a.u.
B	2s1p	24.498	1.0142	0.7328	3.0267	0.9430	0.5971
	4s2p	24.528	1.0059	0.7466	3.0286	0.9333	0.5933
	5s4p	24.529	1.0061	0.7457	3.0249	0.9320	0.5925
	6s4p	24.529	1.0061	0.7458	3.0251	0.9320	0.5925
N	2s1p	54.269	1.0123	5.5125	20.129	6.2993	2.6683
	4s2p	54.398	1.0057	5.6315	20.128	6.1503	2.6506
	5s4p	54.401	1.0059	5.6289	20.111	6.1406	2.6464
	6s4p	54.401	1.0059	5.6291	20.111	6.1406	2.6464
Na	3s1p	161.12	1.0348	0.2265	3.1869	1.3856	1.3324
	6s2p	161.85	1.0143	0.2629	3.3000	1.4185	1.3481
	7s3p	161.86	1.0134	0.2666	3.3110	1.4215	1.3492
	8s5p	161.86	1.0128	0.2673	3.3154	1.4232	1.3508
Li	6s	7.4327	1.0483	0.2088_4	1.0362	0.3083_9	0.2899_9
	6s W[a)]	7.4327	1.0484	0.2087_8	1.0362	0.3083_8	0.2900_0
	6s RSW[b)]	7.4327	1.0484	0.2087_8	1.0361	0.3083_5	0.2899_6
	12s RSW	7.4327	1.0484	0.2088_2	1.0362	0.3083_7	0.2899_8

a) Weiss' basis, Ref. 16. b) Roothaan, Sachs, and Weiss' basis, Ref. 17.

strange at first sight, it is easily understood that such results are quite probable and no strange. The spin virial ratio need not to vary in parallel with the state energy and further it now tends to the limit other than unity.

In Table 2 we inquire into the behavior of the spin virial ratio in different systems and in their isoelectronic sequences for the restricted case. The most remarkable feature is that the ratio has comparatively small deviation from unity in the isoelectronic systems of N and B. This is reasonably ascribed to the fact that the influence of the spin restriction is indirect in these systems, the p-symmetry orbital being purely singly occupied. In the Li-isoelectronic sequence we see that the spin virial ratio becomes close to unity as the nuclear charge increases, but this inclination is not general in the results for the other isoelectronic sequences. We should not make such a hasty deduction as "the tighter is the electronic cloud, the less effective is the spin polarization." The change of Ω_s in the isoelectronic sequences is complicatedly affected by the quality of the basis set and the constraint of the spin restriction.

Turning to the unrestricted case, we examine the spin virial ratio in different systems with the variation of the basis set size in Table 3. Again a gap is observed between the single- and double-zeta results. Here, as expected, the limit of convergence is certainly unity. Generally speaking, the unrestricted

TABLE 2. THE SPIN VIRIAL RATIO IN ISOELECTRONIC SYSTEMS (*Restricted*)

System	Basis	$-E$/a.u.	Ω_s	$\overline{\Delta T}$/a.u.	$-\overline{\Delta V}$/a.u.	$\overline{\Delta W}$/a.u.	$\overline{\Delta X}$/a.u.
Li	6s W	7.4327	1.0484	0.2088	1.0362	0.3084	0.2900
Be$^+$	6s W	14.277	1.0348	0.7020	2.4292	0.5127	0.4636
B^{2+}	6s W	23.376	1.0266	1.4527	4.3160	0.7079	0.6253
C^{3+}	6s W	34.726	1.0214	2.4566	6.7013	0.9000	0.7828
B	5s4p	24.529	1.0061	0.7457	3.0249	0.9320	0.5925
C$^+$	5s4p	37.292	1.0094	1.5812	5.3123	1.3347	0.7854
N^{2+}	5s4p	52.816	1.0088	2.6636	8.0576	1.7164	0.9670
O^{3+}	5s4p	71.095	1.0079	3.9963	11.289	2.0898	1.1437
C$^-$	5s5p	37.709	1.0006	2.8379	12.044	4.3184	2.0468
N	5s4p	54.401	1.0059	5.6289	20.111	6.1404	2.6464
O$^+$	5s4p	74.373	1.0066	9.1330	29.416	7.8283	3.2019
F^{2+}	5s4p	97.609	1.0063	13.384	40.151	9.4725	3.7405
Na	7s3p	161.86	1.0134	0.2666	3.3110	1.4215	1.3492
Mg$^+$	7s3p	199.37	1.0186	0.7429	5.4628	2.0662	1.8831
Al^{2+}	7s3p	241.03	1.0194	1.3496	7.6631	2.6050	2.3064
Si^{3+}	6s3p	286.82	1.0186	2.0770	10.024	3.1035	2.6888

TABLE 3. VARYING OF THE SPIN VIRIAL RATIO WITH BASIS SETS (*Unrestricted*)

System	Basis	$-E$/a.u.	Ω_v	Ω_s	$\overline{\Delta T}$/a.u.	$-\overline{\Delta V}$/a.u.	$\overline{\Delta W}$/a.u.	$\overline{\Delta X}$/a.u.
Li	2s	7.41848	1.00000	1.01539	0.22671	1.05135	0.30658	0.28436
	4s	7.43274	1.00001	1.00052	0.23671	1.06787	0.30848	0.28571
	5s	7.43275	1.00000	1.00081	0.23655	1.06759	0.30844	0.28567
	6s	7.43275	1.00000	1.00050	0.23682	1.06794	0.30845	0.28561
B	2s1p	24.4984	1.00001	1.01424	0.73285	3.02665	0.94295	0.59713
	4s2p	24.5281	1.00001	0.99630	0.79139	3.11632	0.95054	0.58886
	5s4p	24.5293	1.00000	1.00005	0.78189	3.10128	0.94859	0.58885
	6s4p	24.5293	1.00000	1.00005	0.78435	3.10867	0.95035	0.58953
N	2s1p	54.2689	1.00001	1.01235	5.51251	20.1288	6.29935	2.66832
	4s2p	54.4011	1.00002	0.99834	5.89470	20.6020	6.23750	2.59467
	5s4p	54.4038	0.99994	1.00067	5.85057	20.5339	6.22763	2.59731
	6s4p	54.4045	1.00000	1.00002	5.88815	20.6154	6.24400	2.59481
Na	3s1p	161.124	1.00001	1.03479	0.22654	3.18684	1.38561	1.33238
	6s2p	161.850	0.99997	0.98333	0.28987	3.33622	1.42229	1.34385
	7s3p	161.859	1.00000	0.98964	0.27936	3.32259	1.42073	1.34893
	8s5p	161.859	1.00001	0.99977	0.25937	3.28474	1.41352	1.35261

TABLE 4. THE SPIN VIRIAL RATIO IN ISOELECTRONIC SYSTEMS (*Unrestricted*)

System	Basis	$-E$/a.u.	Ω_v	Ω_s	$\overline{\Delta T}$/a.u.	$-\overline{\Delta V}$/a.u.	$\overline{\Delta W}$/a.u.	$\overline{\Delta X}$/a.u.
Li	6s W	7.43275	1.00001	1.00006	0.23736	1.06859	0.30844	0.28539
Be^+	6s W	14.2775	1.00002	1.00020	0.76390	2.49702	0.51282	0.45610
B^{2+}	6s W	23.3761	1.00001	1.00012	1.54555	4.41571	0.70798	0.61627
C^{3+}	6s W	34.7262	1.00001	1.00006	2.57880	6.83083	0.90001	0.77292
B	5s4p	24.5293	1.00000	1.00005	0.78189	3.10128	0.94859	0.58885
C^+	5s4p	37.2926	0.99999	1.00010	1.64570	5.42579	1.35479	0.77926
N^{2+}	5s4p	52.8163	1.00000	1.00008	2.74665	8.19062	1.73679	0.96007
O^{3+}	5s4p	71.0953	1.00000	1.00003	4.09556	11.4380	2.11001	1.13654
C^-	5s5p	37.7098	0.99994	1.00052	2.93956	12.2831	4.37962	2.02134
N	5s4p	54.4038	0.99994	1.00067	5.85057	20.5339	6.22763	2.59731
O^+	5s4p	74.3764	0.99995	1.00060	9.41548	29.9050	7.91634	3.14616
F^{2+}	5s4p	97.6134	0.99996	1.00048	13.7176	40.6902	9.55958	3.68220
Na	7s3p	161.859	1.00000	0.98964	0.27936	3.32259	1.42073	1.34893
Mg^+	7s3p	199.372	1.00000	0.99302	0.79532	5.52702	2.07072	1.87676
Al^{2+}	7s3p	241.030	1.00000	0.99494	1.44237	7.77862	2.61401	2.29447
Si^{3+}	6s3p	286.821	1.00000	0.99582	2.20720	10.1838	3.11543	2.67239

SCF wave function fulfils the spin virial theorem much more well than the restricted one. It may be interpretable as a reflex of this that the unrestricted calculation often gives excellent estimates for spin-related quantities. As another overall feature we should point out that the unrestricted wave function gives larger $\overline{\Delta T}$ and smaller $\overline{\Delta V}$ than the corresponding restricted one almost exclusively.

Table 4 presents the results for the unrestricted wave functions of the isoelectronic systems of Li, B, N, and Na, complementing Table 2. Though the values of Ω_s in the Na-isoelectronic systems have a little large deviation from unity in comparison with the others, we can say that all the members fulfil the spin virial theorem fairly well, taking it into consideration that the basis set used are optimized for the restricted calculation. Comparison between Tables 2 and 4 manifests that the spin restriction is surly a severe constraint.

Concluding Remarks

The spin virial theorem is thought to have both the practical and conceptual significance. The former results from the validity for examining approximate wave functions, being accorded with our original motivation, and the latter consists in the clear recognition of the fact that the motion of electrons in the different spin state is regulated in the stationary state so as to maintain the specific balance represented by the theorem. This recognition is quite fundamental and no less important than the practicability. It is also to be emphasized that the spin virial theorem as well as the spin polarization potential, which is indispensable for the theorem, is not an artificial but natural conception describing a leading feature of the electronic structure.

The idea of specifying the spin state of an operator in the hypervirial theorem seems to be fruitful. We would like to regard the present theorem as the inception of the spin-related theorems derivable from the hypervirial theorem. Moreover, noting that the virial and the spin virial theorems correspond to the Pauli matrices σ_0 and σ_z, respectively, we have certain possibilities of generalization to the other Pauli matrices with appropriate choice of an operator, provided that the Hamiltonian is not spin-conservative.

An extension of the present theorem to the molecular system is conceptually straightforward, and indeed no essential difficulty is met in the formulation using the hypervirial theorem. Nevertheless, we have much to be considered: There are some nuclear-coordinate derivatives that do not vanish even in an equilibrium position. The actual calculation of the spin polarization potential is, of course, very troublesome.

Finally, we would like to add that the spin virial theorem is completely quantum-mechanical, having no classical counterpart, in striking contrast to the virial theorem.

Appendix I

What is to be noted is that the spin state is specified but that we still have the completeness

$$\sum_j \phi_{j\sigma}(\boldsymbol{r}_1)\phi^*_{j\sigma}(\boldsymbol{r}_2) = \delta(\boldsymbol{r}_1-\boldsymbol{r}_2). \tag{69}$$

By virtue of this, for example, it is found that

$$[T_\sigma,\ G_\sigma] = \sum_{jkl}(t_{jl\sigma}g_{lk\sigma}-g_{jl\sigma}t_{lk\sigma})a^\dagger_{j\sigma}a_{k\sigma}$$
$$= \frac{\mathrm{i}}{2}\sum_{jk}\int\phi^*_{j\sigma}(\boldsymbol{r})[\nabla^2,\ \boldsymbol{r}\cdot\nabla]\phi_{k\sigma}(\boldsymbol{r})\mathrm{d}v\, a^\dagger_{j\sigma}a_{k\sigma}. \tag{70}$$

Hence we have only to use the well-known relation

$$[\nabla^2,\ \boldsymbol{r}\cdot\nabla] = 2\nabla^2. \tag{71}$$

Likewise

$$[1/r,\ \boldsymbol{r}\cdot\nabla] = 1/r \tag{72}$$

suffices for the case of V_σ. For the two-electron operator, again by virtue of the above completeness, we have

$$[W_{\sigma\tau},\ G_\sigma] = (1+\delta_{\sigma\tau})\frac{1}{2}$$
$$\times\sum_{jklmn}(w^{jn\sigma}_{lm\tau}g_{nk\sigma}-g_{jn\sigma}w^{nk\sigma}_{lm\tau})a^\dagger_{j\sigma}a^\dagger_{l\tau}a_{m\tau}a_{k\sigma}$$
$$= -(1+\delta_{\sigma\tau})\frac{\mathrm{i}}{2}\sum_{jklm}\iint\phi^*_{j\sigma}(\boldsymbol{r}_1)\phi^*_{l\tau}(\boldsymbol{r}_2)[1/r_{12},\ \boldsymbol{r}_1\cdot\nabla_1]$$
$$\times\ \phi_{m\tau}(\boldsymbol{r}_2)\phi_{k\sigma}(\boldsymbol{r}_1)\mathrm{d}v_2\mathrm{d}v_1\, a^\dagger_{j\sigma}a^\dagger_{l\tau}a_{m\tau}a_{k\sigma}. \tag{73}$$

Calculating the commutator in the integrand as

$$[1/r_{12},\ \boldsymbol{r}_1\cdot\nabla_1] = (r_1^2-\boldsymbol{r}_1\cdot\boldsymbol{r}_2)/r_{12}^3$$
$$= (1/r_{12}+(r_1^2-r_2^2)/r_{12}^3)/2, \tag{74}$$

we reach the resultant.

Appendix II

The crucial point is that the definition of the scaled state with the unitary transformation[6,8]

$$|\eta\theta\rangle = \exp(-\mathrm{i}(G_\uparrow+G_\downarrow)\eta-\mathrm{i}(G_\uparrow-G_\downarrow)\theta)|\mathrm{O}\rangle \tag{75}$$

immediately leads to

$$\frac{\partial}{\partial\eta}\langle\eta\theta|H|\eta\theta\rangle = -\mathrm{i}\langle\eta\theta|[H,\ G_\uparrow+G_\downarrow]|\eta\theta\rangle \tag{76}$$

and

$$\frac{\partial}{\partial\theta}\langle\eta\theta|H|\eta\theta\rangle = -\mathrm{i}\langle\eta\theta|[H,\ G_\uparrow-G_\downarrow]|\eta\theta\rangle. \tag{77}$$

If the unscaled state $|\mathrm{O}\rangle$ is written in the expanded form (Eqs. 44 and 45), we have

$$|\eta\theta\rangle = \sum_M C_M\prod_{j^\sigma\in M}a^\dagger_{j\sigma}(\mu_\sigma)|\text{vacuum}\rangle, \tag{78}$$

where

$$a^\dagger_{j\sigma}(\mu_\sigma) = \exp(-\mathrm{i}G_\sigma\mu_\sigma)a^\dagger_{j\sigma}\exp(\mathrm{i}G_\sigma\mu_\sigma) \tag{79}$$

with

$$\mu_\sigma = \eta + \kappa_\sigma\theta, \tag{80}$$

because $a^\dagger_{j\sigma}$ is commutative with $G_{\bar\sigma}$ and because

$$\exp(-\mathrm{i}G_\sigma\mu_\sigma)|\text{vacuum}\rangle = |\text{vacuum}\rangle. \tag{81}$$

The unitarity allows us to put

$$a_{j\sigma}(\mu_\sigma) = \sum_k u_{jk\sigma}(\mu_\sigma)a_{k\sigma} \tag{82}$$

with

$$u_{jk\sigma}(\mu_\sigma) = \int\phi^*_{j\sigma}(\boldsymbol{r})\phi_{k\sigma}(\boldsymbol{r}:\mu_\sigma)\mathrm{d}v, \tag{83}$$

where $\phi_{j\sigma}(\boldsymbol{r}:\mu_\sigma)$ is the spatial orbital associated with $a^\dagger_{j\sigma}(\mu_\sigma)$ and $a_{j\sigma}(\mu_\sigma)$. From the differential equation

$$\frac{\partial}{\partial\mu_\sigma}a_{j\sigma}(\mu_\sigma) = -\mathrm{i}[G_\sigma,\ a_{j\sigma}(\mu_\sigma)]$$
$$= \mathrm{i}\sum_k g_{jk\sigma}a_{k\sigma}(\mu_\sigma) \tag{84}$$

we can extract the equation for the orbital

$$\frac{\partial}{\partial\mu_\sigma}\phi_{j\sigma}(\boldsymbol{r}:\mu_\sigma) = \frac{1}{2}(\boldsymbol{r}\cdot\nabla+\nabla\cdot\boldsymbol{r})\phi_{j\sigma}(\boldsymbol{r}:\mu_\sigma). \tag{85}$$

It follows immediately that

$$\phi_{j\sigma}(\boldsymbol{r}:\mu_\sigma) = \exp(3\mu_\sigma/2+\mu_\sigma\boldsymbol{r}\cdot\nabla)\phi_{j\sigma}(\boldsymbol{r}), \tag{86}$$

which is readily proved to be identical with our scaled orbitals.

Appendix III

We can analytically integrate the matrix element of the spin polarization potential

$$P = \iint\rho_1(\boldsymbol{r}_1)\rho_2(\boldsymbol{r}_2)((r_1^2-r_2^2)/r_{12}^3)\mathrm{d}v_2\mathrm{d}v_1 \tag{87}$$

rather easily when one of ρ_1 and ρ_2 is spherically symmetric. The analytic integration is not only useful in actual calculation but also instructive because it reveals a latent characteristic of the spin polarization potential. Now we assume ρ_2 is spherically symmetric; $\rho_2(\boldsymbol{r}_2)=\rho_2(r_2)$. Letting the direction of z axis of the second coordinates coincide with that of $\boldsymbol{r}_1$, we change the integration variable θ_2 with r_{12}. Then we have

$$P = 2\pi\int\mathrm{d}v_1\int_0^\infty\mathrm{d}r_2\rho_1(\boldsymbol{r}_1)\rho_2(r_2)r_1^{-1}r_2(r_1^2-r_2^2)\int_{|r_1-r_2|}^{r_1+r_2}\mathrm{d}r_{12}r_{12}^{-2}$$
$$= I_{r_1>r_2} - I_{r_2>r_1} \tag{88}$$

with

$$I_{r_1>r_2} = 4\pi\int\mathrm{d}v_1\rho_1(\boldsymbol{r}_1)r_1^{-1}\int_0^{r_1}\mathrm{d}r_2\rho_2(r_2)r_2^2 \tag{89}$$

and

$$I_{r_2>r_1} = 4\pi\int\mathrm{d}v_1\rho_1(\boldsymbol{r}_1)\int_{r_1}^\infty\mathrm{d}r_2\rho_2(r_2)r_2. \tag{90}$$

These integrals are already familiar. They appear in the calculation of the matrix element of the Coulomb-type electron repulsion integral

$$I = \iint\rho_1(\boldsymbol{r}_1)\rho_2(\boldsymbol{r}_2)(1/r_{12})\mathrm{d}v_2\mathrm{d}v_1, \tag{91}$$

which can be arranged as

$$
\begin{aligned}
I &= 2\pi\int \mathrm{d}v_1\int_0^{\infty}\mathrm{d}r_2\rho_1(\boldsymbol{r}_1)\rho_2(r_2)r_1^{-1}r_2\int_{|r_1-r_2|}^{r_1+r_2}\mathrm{d}r_{12} \\
&= I_{r_1>r_2} + I_{r_2>r_1} \qquad (92)
\end{aligned}
$$

to clarify an intimate connection between P and I.. Besides the density built of s-symmetry orbitals we have a few types of spherically symmetric densities, say, the sum like $p_x^2+p_y^2+p_z^2$; the above treatment is widely practical.

References

1) M. Born, W. Heisenberg, and P. Jordan, *Z. Phys.*, **35**, 557 (1926); B. N. Finkelstein, *ibid.*, **50**, 293 (1928).

2) V. Fock, *Z. Phys.*, **63**, 855 (1930).

3) P.-O. Löwdin, *J. Mol. Spectrosc.*, **3**, 46 (1959); this contains a satisfactory bibliography of the fundamental works on the subject up to 1958.

4) S. T. Epstein, "The Variation Method in Quantum Chemistry," Academic Press, New York (1974), Section 20 and the references cited therein.

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

6) S. T. Epstein and J. O. Hirschfelder, *Phys. Rev.*, **132**, 1495 (1961).

7) J. O. Hirschfelder and C. A. Coulson, *J. Chem. Phys.*, **36**, 941 (1962).

8) S. T. Epstein, "The Variation Method in Quantum Chemistry," Academic Press, New York (1974), Section 16 and the references cited therein.

9) M. Isihara, *Bull. Chem. Soc. Jpn.*, **54**, 3312 (1981).

10) P.-O. Löwdin, *Phys. Rev.*, **97**, 1471 (1955).

11) The scaling dependent on the spin is a two-parameter scaling as an extension of the usual virial scaling. Aside from miscellaneous incorporations of variation parameters in the early days of quantum chemistry, we have a remarkable example of a several-parameter scaling as an extension of the virial scaling in W. J. Meath and J. O. Hirschfelder, *J. Chem. Phys.*, **39**, 1135 (1963). See Ref. 4 also.

12) "Different bases for different spins" is included in "different bases for different orbitals," which is not very new; for example, M. T. Marron, N. C. Handy, R. G. Parr, and H. J. Silverstone, *Int. J. Quantum Chem.*, **4**, 245 (1970); S. Huzinaga and K. Hirao, *J. Chem. Phys.*, **66**, 2157 (1977).

13) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951); *ibid.*, **32**, 179 (1960); C. C. J. Roothaan and P. S. Bagus, *Methods in Compt. Phys.*, **2**, 47 (1963).

14) J. A. Pople and R. K. Nesbet, *J. Chem. Phys.*, **22**, 571 (1954).

15) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

16) A. W. Weiss, *Astrophys. J.*, **138**, 1262 (1963).

17) C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.*, **32**, 186 (1960).

18) It is, of course, possible for the "sufficient" configuration interaction wave function to satisfy the spin virial theorem, even if the wave function is constructed from restricted spin orbitals.