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phosphor) molecules may be located and that these sites differ in local vibrational properties and hence in thermal quenching coefficient. Although this view does not seem to conflict with any of the experimental evidence presented, the relationship between the thermal quenching of phosphorescence and the polymer environment does not appear to be understood on a theoretical level; therefore comparisons with theory cannot be made.

Conclusions

Several conclusions can be drawn from these data without further analysis. The time dependence of decay rate in PBA in the rubbery phase is seen to have a plateau of uniform rate followed by a tail of varying rate extending to the limits of observability. The existence of a plateau in $k(t)$ implies that there are a large number of sites having the same rate constant, if the statistical interpretation of the previous section is

valid. The "tail" coincides almost perfectly with that observed in PMMA at corresponding temperatures, implying that glass-like regions continue to exist in the rubbery phase. A comparison of residual intensity leads to the conclusion that perhaps 10^{-5} part by volume of PBA maintains the glassy phase microstructure at 20° . The temperature dependence of rate constants in PMMA clearly indicates that considerable variations in microstructure exist even at -120° , but more work needs to be done to clarify the nature of the interaction which leads to nonradiative quenching of the triplet state in such an environment before specific deductions based on these observations can be made.

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Scaling in Isoelectronic Molecules

by Jerry Goodisman¹

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A modification of a scaling method introduced for atoms by Ellison enables one to use expectation values calculated for one molecule in calculations of the energy of a second molecule isoelectronic to the first. In going from H_2 to He_2^{2+} , the results are only fair, but in going from LiF to BeO, the results are sufficiently good to allow prediction of equilibrium distance and several expectation values as well as energy. The dipole moment is a notable exception, which reveals one basic dissimilarity between the two molecules, the ionic character. LiF dissociates to ions, BeO to neutral atoms, causing our method to break down at large internuclear distance. The inverse scaling transformation, from BeO to LiF, is also accomplished, with similar results.

In an *a priori* molecular calculation, physical intuition may help in choosing the form for a trial wave function for variation, but one is very rarely in the position of being able to use the wave function for one system for a calculation on another, however closely they are related physically. For atoms, one can use

such fundamental theorems as the virial and Hellman-Feynman theorems to elucidate relations between wave functions for various different systems.² Ellison

- (1) Part of research supported by National Science Foundation.
- (2) For example, P.-O. Löwdin, *J. Mol. Spectry.*, **3**, 46 (1959).

and Huff³ have taken advantage of a scaling procedure, closely related to that used in Fock's proof of the virial theorem,⁴ to calculate the energy of an atomic system from one isoelectronic to it. Tests of the method for various cases^{5b} show impressive agreement.

It is well known that, for molecules, when the usual Born-Oppenheimer separation is used and electronic wave functions are calculated with the nuclei fixed, the virial theorem does not hold in its simple form.⁵⁻⁷ Hirschfelder and Kincaid⁶ have given one way of modifying this theorem, and this suggests a corresponding modification of Ellison's procedure for use in molecules. We first sketch out the arguments of Hirschfelder-Kincaid and Ellison, then formulate the new procedure and apply it to simple cases.

Let $\psi_1(r;R)$ be a wave function for a molecule. We denote all the electronic coordinates by small r and all the nuclear coordinates, which enter as parameters in the usual treatment, by capital R . If we scale (*i.e.*, multiply) *all* coordinates by a parameter, s , we get the scaled wave function $\psi_{1s}(r;R) = s^{3n/2}\psi_1(sr,sR)$. The $s^{3n/2}$ is the correct normalizing factor where n is the number of electrons. We do not integrate over nuclear coordinates in computing norms and expectation values. It is straightforward to show by changing variables in the integrals^{2,3a,6} that $T_s(R) = s^2T_1(sR)$ and $V_s(R) = sV_1(sR)$, where the T 's are expectation values of the kinetic energy and the V 's expectation values of the potential energy. The R or sR in parentheses means this is computed with the internuclear distance held fixed at R or sR , while the subscript 1 or s indicates the use of ψ_1 or ψ_{1s} for the calculation. We find the value of s , s_0 , which minimizes $E_s(R) = T_s(R) + V_s(R)$. If ψ_1 is the exact wave function, s_0 must equal 1. Then, at the equilibrium R , the simple virial theorem holds⁶; at some other R , Slater's modification⁵ will hold.

Now the potential energy consists of three parts

$$V_s(R) = C_s(R) + L_s(R) + M_s(R)$$

and similarly for V_1 , where the three parts are the expectation values of the electron-electron, electron-nucleus, and nucleus-nucleus Coulombic interactions. We want to use the scaled wave function for one molecule for calculation on another molecule isoelectronic with it and related to it by having all nuclear charges multiplied by a constant Z . Then $C_s(R)$ is unchanged, $L_s(R)$ is multiplied by Z , and $M_s(R)$ is multiplied by Z^2 . The expectation value of the energy, using the scaled wave function for the first molecule and the Hamiltonian for the second, is

$$\bar{E}_s(R) = s^2T_1(sR) + sC_1(sR) + ZsL_1(sR) + Z^2sM_1(sR)$$

If we minimize $E_s(R)$ with respect to s , holding sR fixed equal to a constant R_0 , Hirschfelder and Kincaid⁶ note that we will always get an improvement on the energy, but, with sR fixed and s in general different from 1, we will be calculating the energy for the system at $R = R_0/s_0$. This is also true if we minimize $\bar{E}_s(R)$. One finds easily

$$s_0 = [2T_1(sR)]^{-1}[-C_1(sR) - ZL_1(sR) - Z^2M_1(sR)]$$

and the new energy equals

$$\bar{E}_{s_0}(R) = -[4T_{s_0}(R_0)]^{-1}[C_{s_0}(R_0) + ZL_{s_0}(R_0) + Z^2M_{s_0}(R_0)]^2 = -T_{s_0}(R)$$

The last relation expresses the fact that the virial theorem is being satisfied by the scaled function with the Hamiltonian for the second molecule. The case $Z = 1$ is of course the usual case, where a molecular wave function is improved by scaling.

We consider as our unscaled function that for H_2 at its equilibrium internuclear distance, $1.4a_0$. According to the Kolos-Roothaan 40-term function⁸ the total energy in atomic units here is -1.174440 , the total potential energy is -2.349279 (electron-electron potential energy = 0.58737 , nucleus-nucleus potential energy = 0.714286 , electron-nucleus potential energy = -3.65094), and the electronic kinetic energy = 1.174839 . We use this for the He_2^{2+} ion, for which good wave functions are also available.⁸ By the above equations, we find $s_0 = 1.64165$ so that $R = R_0/s_0 = 0.85280$. The new energy is calculated as -3.16621 atomic units. Kolos and Roothaan⁸ do not give the energy at this distance, but by fitting the first five points in their Table XI, $\alpha = 1.75$, to a parabola, we find that the correct answer is -3.433 atomic units.

Note that the variational principle holds here; our answer must be too high. A series of similar calculations with H_2 data for different internuclear distances would yield a series of results for He_2^{2+} , but there is not sufficient data in ref. 8 to make this possible. The agreement is not very good; Ellison^{3b} found, however, that agreement for atoms was better for smaller ratios of nuclear charges, which is reasonable.

There is no reason to limit this kind of treatment to

(3) (a) F. O. Ellison, *J. Chem. Phys.*, **37**, 1414 (1962); (b) F. O. Ellison and N. T. Huff, *ibid.*, **39**, 2051 (1963).

(4) V. Fock, *Z. Physik*, **63**, 855 (1930).

(5) J. C. Slater, *J. Chem. Phys.*, **1**, 687 (1933).

(6) J. O. Hirschfelder and J. F. Kincaid, *Phys. Rev.*, **52**, 658 (1937).

(7) C. A. Coulson and R. P. Bell, *Trans. Faraday Soc.*, **41**, 141 (1945); A. C. Hurley, *Proc. Roy. Soc. (London)*, **A226**, 170 (1954).

(8) W. Kolos and C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 219 (1960).

Table 1: Calculations for LiF \rightarrow BeO^a

$sR(a_0)$	$T_1(sR)$	$C_1(sR)$	$L_1^A(sR)$	$L_1^B(sR)$	$M_1(sR)$	s_0	$\frac{sR(a_0)}{s_0}$	\bar{E}_{s_0}
1.60	109.52710	59.46506	-34.37385	-257.7301	16.87500	0.892291	1.79314	-87.2036
2.10	107.92227	56.59302	-30.44886	-253.7509	12.85714	0.900295	2.33257	-87.4744
2.35	107.47837	55.49567	-28.99485	-252.3926	11.48936	0.902024	2.60525	-87.4495
2.60	107.19787	54.60136	-27.79869	-251.3504	10.38461	0.902903	2.87960	-87.3914
2.85	107.02626	53.87033	-26.80035	-250.5460	9.47368	0.903254	3.15526	-87.3193

^a Expectation values in columns 1-5 obtained from calculation VIII.A of McLean, ref. 9. All energies in atomic units. See text for abbreviations.

cases where the isoelectronic molecules are related by symmetric scaling of the nuclear charges. Let us increase the charge on nucleus A by a factor Z_A and the charge on nucleus B by Z_B (generally, one of these will be >1 and the other <1). Minimizing the energy with respect to the scaling parameter s while holding $sR = R_0$ fixed yields

$$s_0 = [2T_1(sR)]^{-1}[-C_1(sR) - Z_A L_1^A(sR) - Z_B L_1^B(sR) - Z_A Z_B M_1(sR)]$$

where we write L_1^A for the expectation value of the interaction of the electrons with nucleus A, and L_1^B for that for nucleus B. The energy obtained is equal to $-s_0^2 T_1(sR)$.

In attempting to apply this to molecules, one finds that the literature offers a paucity of published calculations with sufficient data for our procedure. We require the expectation values of total energy, kinetic energy, and electron-nucleus interaction for each nucleus. McLean⁹ has performed a series of LCAO-SCF calculations on the LiF molecule and tabulated many important expectation values. We employ these for calculations on the isoelectronic BeO molecule. Furthermore, Yoshimine¹⁰ has performed limited basis SCF calculations for BeO, and we can use his results in several ways, to be indicated below. Here, Z_A (referring to Li \rightarrow Be) is $4/3$ and Z_B (referring to F \rightarrow O) is $8/9$. The expectation values used come from McLean's calculation VIII.A and appear, with the results, in Table I. We have used only values of sR ($=R_{\text{LiF}}$) such that R ($=R_{\text{BeO}}$) falls near the equilibrium value.

From data in Herzberg,¹¹ we estimate the true total energy of BeO at the equilibrium distance as -89.784 a.u. Our energy at the minimum, -87.478 , is off by 2.5%. We have fitted the five calculated energies to a parabola in the internuclear distance.¹² The result is an equilibrium distance of $2.55 \pm 0.01a_0$ and a force constant of 0.88 ± 0.20 a.u./ a_0^2 or 13.7×10^5 dynes/

cm.², to be compared with the experimental¹¹ $2.5147a_0$ and 7.5089×10^5 dynes/cm.².

Now we refer to the calculations of Yoshimine¹⁰ on BeO, similar in scope to McLean's for LiF. This enables us, first, to decide whether the errors in the quantities calculated above are to be considered large and, second, to compare a wider variety of scaled expectation values (whose calculation we discuss below), for some of which experimental data are not available, with their values as predicted by an *a priori* calculation on BeO. Finally, the expectation values furnished by Yoshimine allow us to accomplish the scaling transformation from BeO to LiF.

With reference to the first point, we note that Yoshimine's calculated equilibrium internuclear distance for BeO is $2.4378a_0$, *i.e.*, 3% too low, whereas ours is about 1.05% too high. His calculated force constant (proportional to the square of the frequency) is high by a factor of 1.2, ours by a factor of 1.8.

The calculation of expectation values with the scaled function is straightforward. Let $f(r_e)$ be a function homogeneous of degree i in the electronic coordinates, *i.e.*, $f(s\vec{r}_e) = s^i f(\vec{r}_e)$. The electron-electron potential energy, for instance, is homogeneous of degree -1 ; the kinetic energy operator for the electrons may be

(9) A. D. McLean, *J. Chem. Phys.*, **39**, 2653 (1963).

(10) M. Yoshimine, *ibid.*, **40**, 2970 (1964).

(11) G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1950, pp. 458, 509.

(12) Strictly speaking, these are not the points we should be fitting to get the equilibrium distance and force constant. What we really would like to have is a contour map, giving calculated energy as a function of both scaling parameter s and BeO internuclear distance R . We should then obtain the best scaling parameter and minimum energy for each internuclear distance and fit these points to a parabola. The path through the minima would not, in general, be parallel to either the s or the R axis. What we are doing now is finding the best scaling parameter and minimum energy on the hyperbolae $sR = 1.60, 1.85, 2.10$, etc., and fitting these minima to a parabola. We could, in principle, interpolate on each hyperbola to get energies at any value of R , then use these to find the best energy and scaling parameter for each R . This interpolation turns out to be far from reliable and seems to lead to only small changes in the equilibrium distance and force constant for LiF \rightarrow BeO.

Table II: Expectation Values for LiF \rightarrow BeO

$R_{\text{LiF}} =$ $sR(a_0)$	$R_{\text{BeO}} =$ $sR(a_0)$ s_0	E in a.u. by scaling	E by direct calcn. ^a	$\langle r^2 \rangle_{\text{Be}}$ by scaling, a_0^2	$\langle r^2 \rangle_{\text{Be}}$ by calcn. ^a	$\langle 3z^2 - r^2 \rangle_{\text{Be}}$ by scaling	$\langle 3z^2 - r^2 \rangle_{\text{Be}}$ by calcn. ^a	Dipole moment in a.u., by scaling	Dipole moment in a.u., by calcn. ^a
1.60	1.79314	-87.204		49.3824		61.9975		2.9337	
	1.80		-89.153		48.3478		55.4156		2.1593
	2.150		-89.404		61.1407		79.4192		2.5121
2.10	2.33257	-87.474		71.2409		104.4469		4.1735	
	2.400		-89.444		71.4815		99.2673		2.7467
	2.476		-89.444		74.8265		105.7250		2.8114
	2.550		-89.440		78.1726		112.1944		2.8697
2.35	2.60525	-87.449		84.3566		130.445		4.6928	
	2.800		-89.412		90.0982		135.2481		3.0072
2.60	2.87960	-87.391		98.9682		159.618		5.2015	
	3.050		-89.373		102.8409		159.5814		2.9401
2.85	3.15526	-87.319		115.6269		191.976		5.7099	
	3.800		-89.300		145.1189		238.7916		1.7578

^a SCF-LCAO calculations by M. Yoshimine, *J. Chem. Phys.*, **40**, 2970 (1964).

considered as homogeneous with $i = -2$. Note that the complete potential energy function is not homogeneous in the electronic coordinates alone. Denoting by $\langle f \rangle_s^R$ the expectation value of f at an internuclear distance R , calculated with the scaled wave function, and $\langle f \rangle_1^{sR}$ the expectation value calculated with the unscaled function at internuclear distance sR , we have

$$\langle f \rangle_s^R = \langle f \rangle_1^{sR} / s^i$$

This is shown by a simple change of variables in the integral, as in the proofs of the virial theorem itself.^{4,6}

In Table II, we have used this to calculate $\langle r_{\text{Be}}^2 \rangle_s^R$ and $\langle 3z_{\text{Be}}^2 - r_{\text{Be}}^2 \rangle_s^R$ from $\langle r_{\text{Li}}^2 \rangle_1^{sR}$ and $\langle 3z_{\text{Li}}^2 - r_{\text{Li}}^2 \rangle_1^{sR}$. The values of R and s from Table I have been employed. For $\langle r^2 \rangle_{\text{Be}}$, we get good agreement with Yoshimine's calculations,¹¹ to a few per cent. The average or expectation value of the square of a distance of an electron from a nucleus is a measure of the size of a molecule. It is the size which a scaling factor can adjust, so that we probably should expect good results here. On the other hand, the expectation value of $\langle 3z_{\text{Be}}^2 - r_{\text{Be}}^2 \rangle = 2(z_{\text{Be}}^2 - x_{\text{Be}}^2)$, which is essentially the electronic contribution to the molecular quadrupole moment, is a measure of the shape of the electron distribution. The agreement here is not nearly as good, but still satisfactory. We should expect the agreement in both cases to get progressively worse at large R . For example, with $sR = R_{\text{LiF}} = 4.85$, we calculate an optimum value of $s = 0.90126$. The predicted values of $\langle r_{\text{Be}}^2 \rangle_s^R$ and $\langle 3z_{\text{Be}}^2 - r_{\text{Be}}^2 \rangle_s^R$ are then $302.173a_0^2$ and $565.955a_0^2$. $R = 4.85/0.90126 = 5.38134a_0$. Interpolating in Yoshimine's results, we estimate the correct values to be, respectively,

$250a_0^2$ and $450a_0^2$. The per cent errors are about the same in both, since, for large internuclear distance, $\langle z^2 \rangle \rightarrow \langle r^2 \rangle$.

The dipole moment consists of an electronic part and a nuclear part. The latter can be separated out and calculated exactly, while the former's operator is homogeneous of degree 1. It is, in fact, $\sum_j z_j$, where z_j is the distance of electron j along the internuclear axis from some origin. For an electrically neutral molecule, the origin may be chosen arbitrarily, as long as it is used consistently for both the electronic and nuclear parts. Taking it on the Li nucleus, we have $\langle z_{\text{Li}} \rangle = \mu - 9R_{\text{LiF}}$ in atomic units, where μ represents the total dipole moment. Scaling to obtain the expectation value for BeO, we have $\langle z_{\text{Be}} \rangle = \langle z \rangle_{\text{Li}} / s$, to which we must add $8R_{\text{BeO}}$ to get the predicted dipole moment for BeO at an internuclear distance of R_{BeO} . The next to the last column in Table II was obtained in this manner. One can, in fact, show that, for our case, the same answer is obtained for any origin, provided that this origin is defined relative to the internuclear distance and not to some space-fixed system of coordinates. Note that we change the internuclear distance in scaling from LiF to BeO. Thus, take the distance from nucleus 1 to the origin as f times the internuclear distance ($1 = \text{Li, Be}$ and $2 = \text{F, O}$). We find

$$\langle z \rangle = \mu - q_2(1 - f)sR + q_1fsR$$

with q_1 and q_2 the charges on 1 and 2. This gives the dipole moment for the scaled molecule with charges q_1' and q_2' as

$$\begin{aligned} \langle z \rangle / s + q_2(1-f)R - q_1'fR &= \mu/s - \\ (q_2 - q_2')(1-f)R + (q_1 - q_1')fR &= \mu/s + \\ fR(q_2 - q_2' + q_1 - q_1') - (q_2 - q_2')R & \end{aligned}$$

The term depending on f vanishes as long as $q_1 + q_2 = q_1' + q_2'$, *i.e.*, no change in the total nuclear charge between the two isoelectronic molecules. Only for neutral molecules, however, is the dipole moment expected to be independent of origin in the first place.

The agreement for the dipole moment (last two columns of Table II) is poor and gets worse at larger R . This comes from the fact that $\mu_{\text{LiF}} \rightarrow eR$ as $R \rightarrow \infty$, while $\psi_{\text{BeO}} \rightarrow 0$ as $R \rightarrow \infty$. In chemical terms, LiF dissociates into ions and BeO into neutral atoms. The molecules are thus completely different at large R . We see this reflected also in the increasing errors in $\langle r^2 \rangle_{\text{Be}}$ and $\langle 3z^2 - r^2 \rangle_{\text{Be}}$ as R gets large. The dipole moment, which has often been used as the measure of ionic character, is more sensitive to the qualitative differences in bonding between LiF and BeO than either of the above so that errors set in earlier.

Finally, we turn to the problem of rescaling Yo-

shimine's BeO wave function for LiF. Here, $Z_A = 3/4$, $Z_B = 9/8$. Table III, whose construction is similar to that of Table I, shows the results of these calculations. Fitting the points here to a parabola in R , we find the minimum (equilibrium internuclear distance) at $R = 2.387 \pm 0.1a_0$, and a force constant of $0.8194 \text{ a.u./}a_0^2$.¹² The energy at the minimum is -104.4927 . To this we must compare the experimental results— $R_{\text{min}} = 2.955a_0$, $k_f = 0.2069 \text{ a.u./}a_0^2$, $E(R = R_{\text{min}}) = -107.435 \text{ a.u.}$ —as well as the calculated results of McLean— $R_{\text{min}} = 2.8877a_0$, $E(R = R_{\text{min}}) = -106.977 \text{ a.u.}$, $(d^2E/dR^2)_{R=R_{\text{min}}} \cong 0.194 \text{ a.u./}a_0^2$.

In Table IV, the scaling parameters determined in Table III are used for the calculation of expectation values. These are compared to McLean's results. Agreement for $\langle r^2 \rangle_{\text{Li}}$ is good, agreement for $\langle 3z^2 - r^2 \rangle_{\text{Li}}$ is a bit less good, and agreement for the dipole moment is poor. As one might have anticipated, the pattern is inverse to that for LiF \rightarrow BeO (Table II). In this case, the dipole is consistently too low. Here, all the expectation values are too small and get worse at larger R , as the difference in the ionic character of the bonds

Table III: Calculations for BeO \rightarrow LiF^a

$sR(a_0)$	$T_1(sR)$	$C_1(sR)$	$L_1^A(sR)$	$L_1^B(sR)$	$M_1(sR)$	s_0	$\frac{sR}{s_0}(a_0)$	\bar{E}_{s_0}
2.150	90.06195	49.1080	-48.7540	-194.7040	14.8837	1.076711	1.99682	-104.4094
2.400	89.5418	47.7527	-47.0152	-193.0560	13.3333	1.080203	2.22180	-104.4809
2.476	89.4268	47.3844	-46.5520	-192.6264	12.9241	1.080938	2.29060	-104.4887
2.55	89.3307	47.0420	-46.1272	-192.2352	12.5490	1.081542	2.35774	-104.4931
2.80	89.1056	45.9732	-44.8616	-191.0576	11.4286	1.082816	2.58585	-104.4755
3.05	89.0246	44.9570	-43.8372	-190.0088	10.4918	1.083006	2.81624	-104.4171

^a Expectation values in columns 1-5 obtained from calculation c of Yoshimine, ref. 10. Energies in atomic units. See text for abbreviations.

Table IV: Expectation Values for BeO \rightarrow LiF

$R_{\text{BeO}} = sR(a_0)$	$R_{\text{LiF}} = sR/s_0(a_0)$	$E, \text{ a.u.}$		$\langle r^2 \rangle_{\text{Li}}, a_0^2$		$\langle 3z^2 - r^2 \rangle_{\text{Li}}, a_0^2$		Dipole moment, a.u.	
		Scaling	Calcn. ^a	Scaling	Calcn. ^a	Scaling	Calcn. ^a	Scaling	Calcn. ^a
	1.60		-106.2368		39.3174		49.3614		1.0177
2.150		-104.4094		52.7390		68.5058		0.3363	
	2.10		-106.8273		57.7430		84.6575		1.6574
2.400	2.22180	-104.4809		61.2608		85.0737		0.3210	
2.476	2.29060	-104.4887		64.0404		90.4849		0.3103	
	2.350		-106.9240		68.6366		106.1365		1.8830
2.550	2.35774	-104.4931		66.8294		95.9145		0.2956	
2.800	2.58585	-104.4755		76.8434		115.3511		0.1914	
	2.60		-106.9652		80.6820		130.1258		2.0964
3.05	2.81624	-104.4171		87.6807		136.0569		0.1015	
	2.85		-106.9768		93.9270		156.6269		2.3075

^a Calculation is that of A. D. McLean, *J. Chem. Phys.*, **39**, 2653 (1963).

in LiF and BeO gains in importance. The BeO wave function, scaled for LiF, must lead to a dipole moment approaching 0 as R gets very large. This is of course totally unsuited to a description of the ionic LiF molecule.

In fact, BeO and LiF would certainly be considered by a chemist as almost totally dissimilar molecules. This makes it all the more surprising that our scaling allowed us to do so well on the various molecular constants. It is tempting to think that this sort of calculation suffers from disadvantages opposite to those of simple variational calculations; that is, it allows one to do well on the inner shells but describes the valence, or chemical, electrons less adequately.

We must remember that the wave functions we used for LiF and BeO are not exact—errors in the energies run about 0.5%—and that we require several expectation values which are more sensitive than the energy to errors in the wave function.^{8,13} In this connection, the self-consistent field wave function (to which McLean's and Yoshimine's wave functions are approximations) is most suitable for a starting point in the present calculations. Brillouin's theorem¹⁴ guarantees

that one-electron operators, as well as the total energy, have second-order errors when the wave function is in error in first order. The kinetic energy and the electron-nucleus potential energies are one-electron, while the electron-electron repulsion is a difference between the total energy and one-electron operators.

It is unfortunate that there are not more published calculations giving expectation values other than total energy to allow more calculations like those above. An interesting case would be $\text{CO} \rightarrow \text{N}_2$, as the two are often considered to be very similar.¹⁵ If we consider the scaling process to change the "size" of the wave function but not its "shape," we do not anticipate very good results when the nuclear charges are changed too radically.

(13) For instance, P.-O. Löwdin, *Ann. Rev. Phys. Chem.*, **11**, 107 (1960); C. Eckart, *Phys. Rev.*, **36**, 878 (1930). Note, as an example of this, Table XVI of ref. 8.

(14) L. Brillouin, *Actualités Sci. Ind.*, **71**, 159, 160 (1933-1934); C. Möller and M. S. Plesset, *Phys. Rev.*, **46**, 618 (1937); J. Goodman and W. Klemperer, *J. Chem. Phys.*, **38**, 711 (1963); G. G. Hall, *Phil. Mag.*, **6**, 249 (1961).

(15) For example, Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Dover Publications, New York, N. Y., 1964, pp. 136-138.