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Marron-Weare Variational Computation of Energy Differences for Motions of C_2H_6, B_2H_6, $CH_3CH_2^+$, and CH_3BH_2

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The passage of $D_{3d}C_2H_6$ and B_2H_6 toward a D_{2h} bridged structure, and the motion of a methyl proton maintaining C_s symmetry in $C_2H_5^+$ and CH_3BH_2 are described by integral Hellmann-Feynman computations in a Frost floating spherical Gaussian basis. Marron and Weare's variational corrections to the integral Hellmann-Feynman formula for ΔE between states A and B are evaluated with variational functions of the form $\eta(\psi_A/S_{AB}-\psi_B)$ used to refine the state B. An analogous function $\xi(\psi_B/S_{AB}-\psi_A)$ refines state A. Both η and ξ are chosen variationally to minimize Marron and Weare's functional. No obvious advantage of the variational method became apparent in this simple application.

Key word: Marron-Weare variational computation

The integral Hellmann-Feynman theorem developed by Parr [1], $\Delta E = \langle\psi_A|\Delta H|\psi_B\rangle/\langle\psi_A|\psi_B\rangle + \Delta V_{nn}$ has contributed significantly to the qualitative understanding of charge reorganization and energy changes accompanying changes in nuclear position or nuclear charge [2]. The computational history of the integral Hellmann-Feynman formula is not so happy, however. The error in the integral Hellmann-Feynman estimate in energy changes is of the first order in errors of the wave functions ψ_A, ψ_B, and is also highly sensitive to the departure of the overlap $\langle\psi_A|\psi_B\rangle$ from unity. Even estimable wave functions yield erratic estimates of energy changes, according to tests on NH_3, H_2O_2 [3], and He [4] atom. Epstein [5] and Silverstone [6] described conditions under which expectation value differences and integral Hellmann-Feynman estimates agree. In a previous communication [7], we have described the improvement in integral Hellmann-Feynman computational stability accompanying the guarantee of satisfaction of the differential limit of the Hellmann-Feynman formula. Use of a common (AO) basis for the computation of isoelectronic systems also improves the integral Hellmann-Feynman estimate considerably.

In this report we describe an application of Marron and Weare's stationary principle for the energy change [8], which may according to the originators provide a better estimate of ΔE than either expectation value differences or direct integral Hellmann-Feynman computation. This claim was substantiated by results on $He^+ \rightarrow H$ and $H_2^+ \rightarrow H + H^+$ [8].

To approach the idea of a variational refinement of the integral Hellmann-Feynman formula, consider a perturbation expression for ΔE accompanying a shift in nuclear position so that $H_0 \rightarrow H_F = H_0 + V$

$$\Delta E = V_{00} + \langle \psi_0 | V | \psi_0{}^{(1)} \rangle. \tag{1}$$

Here $\psi_0^{(1)}$ is a correction to ψ_0 reflecting the change in Hamiltonian from H_0 to H_F. Requiring that $\langle \psi_0^{(1)} | \psi_0 \rangle = 0$ and that $\psi_0 + \psi_0^{(1)}$ resemble ψ_F, we can write

$$\psi_0^{(1)} \cong \frac{\psi_F}{S_{0F}} - \psi_0. \tag{2}$$

Here $S_{0F} = \langle \psi_0 | \psi_F \rangle$. Inserting this expression for $\psi_0^{(1)}$ in the equation for ΔE, we find

$$\Delta E = V_{00} + \frac{V_{0F}}{S_{0F}} - V_{00} = \frac{V_{0F}}{S_{0F}}. \tag{3}$$

This is just the integral Hellmann-Feynman formula for the change in electronic energy. We gather the impression that if S_{0F} is large, that the integral Hellmann-Feynman formula is equivalent with this special form of second order perturbation theory.

If we do not make the rather special assumption written above for $\psi_0^{(1)}$, but write

$$\psi_0^{(1)} = \eta \left(\frac{\psi_F}{S_{0F}} - \psi_0 \right), \tag{4}$$

we can consider η to be a variational parameter. Minimizing the functional

$$\langle \psi_0^{(1)} | H_0 - E_0 | \psi_0^{(1)} \rangle + 2 \langle \psi_0^{(1)} | V - E_0^{(1)} | \psi_0 \rangle = J(\psi_0^{(1)}) \tag{5}$$

with respect to η, which guarantees satisfaction of the first order perturbation equation to the maximum extent possible in the range of choices for $\psi_0^{(1)}$, we find

$$\eta = \frac{\left(\frac{V_{0F}}{S_{0F}} - V_{00} \right)}{2E_0 - 2\frac{\langle \psi_0 | H_0 | \psi_F \rangle}{S_{0F}}} + \left(\frac{E_F - E_0 - V_{FF}}{S_{0F}^2} \right). \tag{6}$$

This expression will in general be different from unity. Its departure from unity shows an inconsistency between the integral Hellmann-Feynman (iHF) formula and the first terms of the perturbation sequence. Higher terms may improve the perturbation approximation, and may tend to cancel the term proportional to $(1 - \eta)$

$$\begin{aligned}
\Delta E_{pv} &= V_{00} + \eta\left(\frac{V_{0F}}{S_{0F}} - V_{00}\right) \\
&= V_{00} + \frac{\left(\dfrac{V_{0F}}{S_{0F}} - V_{00}\right)^2}{2E_0 - 2\dfrac{\langle\psi_0|H_0|\psi_F\rangle}{S_{0F}} + \left(\dfrac{E_F - E_0 - V_{FF}}{S_{0F}^2}\right)} \\
&= \Delta E_{iHF} + (1-\eta)\left(\frac{V_{0F}}{S_{0F}} - V_{00}\right) \\
&= V_{00} + \frac{(V_{0F} - V_{00}S_{0F})^2}{2S_{0F}^2 E_0 - 2S_{0F}\langle\psi_0|H_0|\psi_F\rangle + E_F - E_0 - V_{FF}}.
\end{aligned} \tag{7}$$

Note that evaluation of this expression requires knowledge of the energy expectation value difference, as well as the two wave functions Ψ_0 and ψ_F. Further the relatively unfamiliar integral $\langle\psi_0|H_0|\psi_F\rangle$ must be evaluated.

We do not pursue this expression further, since it does not make symmetric reference to H_0 and H_F. Instead we turn to the comparable expressions developed by Marron and Weare [8]. In their investigation of the process $H \rightarrow He^+$ and $H_2^+ \rightarrow H + H^+$, they minimized the functionals

$$F(\psi_0^{(1)}) = \left[\langle\psi_F|H_0 - E_0|\psi_0^{(1)}\rangle + \frac{\langle\psi_F|V - (E_F - E_0)|\psi_F\rangle}{S_{0F}}\right]^2 \tag{8a}$$

$$F(\psi_F^{(1)}) = \left[\langle\psi_0|H_F - E_F|\psi_F^{(1)}\rangle - \frac{\langle\psi_0|V - (E_F - E_0)|\psi_0\rangle}{S_{0F}}\right]^2, \tag{8b}$$

with $\psi_0^{(1)}$ and $\psi_F^{(1)}$ variational corrections to ψ_0 and ψ_F respectively. We choose

$$\psi_0^{(1)} = \eta\left(\frac{\psi_F}{S_{0F}} - \psi_0\right), \tag{9a}$$

$$\psi_F^{(1)} = \xi\left(\frac{\psi_0}{S_{0F}} - \psi_F\right), \tag{9b}$$

and minimize $F(\psi_0^{(1)})$ and $F(\psi_0^{(1)})$ with respect to η and ξ.

We obtain the extremum expression for $[\Delta H]$, the variational energy difference:

$$\begin{aligned}
[\Delta H] = \Delta E_{iHF} + \frac{-1}{S_{0F}}\Bigg\{&\frac{(E_F - E_0 - V_{FF})(\langle\psi_0|H_0|\psi_F\rangle - S_{0F}E_0)}{E_F - E_0 - V_{FF} - S_{0F}\langle\psi_0|H_0|\psi_F\rangle - S_{0F}^2 E_0} \\
&- \frac{(E_F - E_0 - V_{00})(\langle\psi_0|H_F|\psi_F\rangle - S_{0F}E_F)}{E_F - E_0 - V_{00} + S_{0F}\langle\psi_0|H_F|\psi_F\rangle + S_{0F}^2 E_F}\Bigg\}.
\end{aligned} \tag{10}$$

If S_{0F} is near unity, the variational correction terms are such that $[\Delta H]$ is stable through first order (*to* second order) in wave function errors insofar as the trial functions $\psi_0^{(1)}$, $\psi_F^{(1)}$ can represent the response of the initial and final systems to the interconversion. The size of the correction reflects the inadequacy of the integral

Table 1. Expectation, integral Hellmann-Feynman, and Marron-Weare variational energy differences[a]

X_0	X_F	S_{0F}	ΔW	Ω_{iHF}	$[\Delta\mathscr{H}]$	ΔV_{nn}
a) B_2H_6						
EQ	0.5	0.6256	1.3818	1.0926	0.4097	−1.3722
0.5	1.0	0.3209	2.0916	1.8385	−3.0571	−2.0977
1.0	1.5	0.8105	0.6759	0.7190	0.7317	−0.6746
EC	ST	0.4307	−0.0135	−0.0105	−0.2855	
b) C_2H_6						
ECL	ST	0.6527	−0.0213	−0.0333	−0.0160	+0.0118
2.0	ST	0.9940	0.2622	0.2666	0.2658	−0.2636
1.5	2.0	0.9720	0.2372	0.2157	0.2202	−0.2651
1.0	1.5	0.9459	0.2504	0.2444	0.2407	−0.3370
0.5	1.0	+0.7338	−0.6750	−0.6865	−0.6588	+0.6134
c) $C_2H_5^+$						
−1.0	EQ	0.9637	0.1276	0.1390	0.1413	−0.1446
−0.5	−1.0	0.9448	0.3144	0.3256	0.3318	−0.3243
0.0	−0.5	0.9099	0.5279	0.5399	0.5584	−0.5270
d) CH_3BH_2						
EQ	−2.25	0.9516	0.1005	0.1071	0.1084	−0.1204
−1.5	EQ	0.9894	0.1862	0.1798	0.1800	−0.1702
−0.75	−1.5	0.9341	0.5750	0.5550	0.5670	−0.5756
+0.0	−0.75	0.8920	0.2875	0.3476	0.3652	−0.3024
+0.75	0.0	0.9698	0.4506	0.4927	0.4881	−0.3655
−0.50	−0.75	0.9896	0.1289	0.1343	0.1346	−0.1344[b]
0.0	−0.5	0.9416	0.1586	0.2130	0.2165	−0.1680
			0.2875	0.3473	0.3511	−0.3024

[a] Differences are $E(X_F)-E(X_0)$, final energies less initial energies. EQ = equilibrium geometry, EC = eclipsed, ST = staggered; X = reaction coordinate defined in text; ΔW = expectation value difference; Ω_{iHF} = integral Hellmann-Feynman estimate; $[\Delta\mathscr{H}]$ = variational estimate; ΔV_{nn} = change in nuclear repulsion energy. X_0, X_F are defined as X coordinates of the migrating hydrogens where the X axis $\parallel$ the vector connecting the heavy atoms. Energy is in Hartrees.

[b] Sums of expectation value differences and nuclear repulsion differences are independent of path, sums of ΔE_{iHF} or $[\Delta\mathscr{H}]$ are not.

Hellmann-Feynman formula and/or the inadequacy of specific variational functions in iHF computations.

In Marron and Weare's illustrations of their variation method, the virial theorem was satisfied by optimizing scale factors. We have chosen floating spherical Gaussian (Lewis or Frost) orbitals as a basis, and the subminimal set described by Frost [9] to represent ψ_0 and ψ_F, because the virial theorem can be satisfied by optimizing scale for rather larger systems than previously treated by Marron and Weare. Further, the differential form of the Hellmann-Feynman theorem can be satisfied by optimizing orbital location.

The curious integrals $\langle\psi_0|H_0|\psi_F\rangle$ and $\langle\psi_0|H_F|\psi_F\rangle$ in which $\langle\psi_0|\psi_F\rangle \neq 0$, involve the orbitals of configuration 0, $(\bar{a}_0)$ and configuration $F, (\bar{b}_F)$. These orbitals are nonorthogonal both within a set $\bar{a}$ or $\bar{b}$, or between sets $\bar{a}$ and $\bar{b}$ ($\langle a_{0i} b_{Fj}\rangle \neq \delta_{ij}$; $\langle a_{0i} a_{0k}\rangle \neq \delta_{ik}$; $\langle b_{0j} b_{0l}\rangle \neq \delta_{jl}$). These integrals can be evaluated by the method of corresponding orbitals [10]. The necessary programs for integral Hellmann-

Feynman calculations, I° perturbation calculations and corresponding orbitals were developed by JKG.

We have assembled extensively but not perfectly optimized floating spherical Gaussian wave functions for the proton transfer motion maintaining a plane of symmetry in $CH_3CH_2^+$ and CH_3BH_2, and for internal rotation and the bridging motion in C_2H_6 and B_2H_6 [these were computed in part by Lucy Cline Weiss as part of a term project in the graduate course "Chemical Applications of Quantum Mechanics"]. The sections of the energy surface were described by expectation values in a perfectly reasonable way. The direct proton transfer in $C_2H_5^+$ was permitted only via a C_{2v} intermediate; proton transfer from C to B in CH_3BH_2 was strongly resisted. Internal rotation in C_2H_6 was opposed by *ca.* 6 kcal/mole, and ethane resisted bridging vigorously. B_2H_6 preferred bridging, but the relative stability of the bridged form was underestimated (CI is apparently necessary to account for this stability) [11].

Our object is to compare expectation value differences, integral Hellmann-Feynman estimates of energy differences, and variational estimates of energy differences for these several motions. Results of these computations are summarized in Tables 1a–d and Figs. 1, 2a–d. These tables contain expectation value differences, integral Hellmann-Feynman estimates, and variational estimates of energy changes, calculated according to Eq.(10). Fig. 1 contains a scattergram of the estimates of ΔE, while Fig. 2 shows potential curves deduced from ΔE computations. The wave functions ψ_0 and ψ_F were obtained by Lewis orbital computations using the program by Frost and Rouse distributed by the Quantum Chemistry Program Exchange [12]. Complete optimization of all structures and functions was permitted, with the constraints of C_s symmetry in $CH_3CH_2^+$ and CH_3BH_2, and C_{2h} symmetry in C_2H_6 and B_2H_6, and specifications of the value

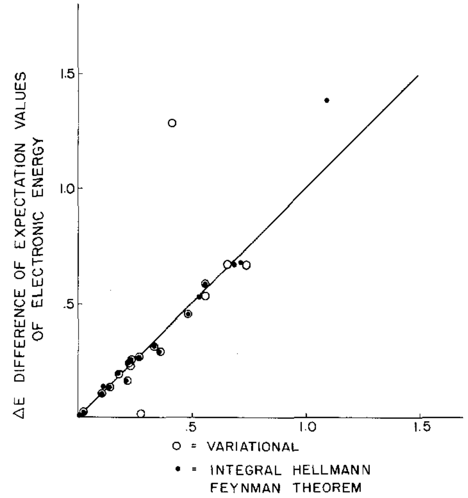

Fig. 1. A plot of the relation of integral Hellmann-Feynman electronic energy changes (points) and variational estimates of electronic energy changes (circles) against expectation value differences shows a fair correlation between the three sets. These energy changes do not include nuclear repulsion energy changes

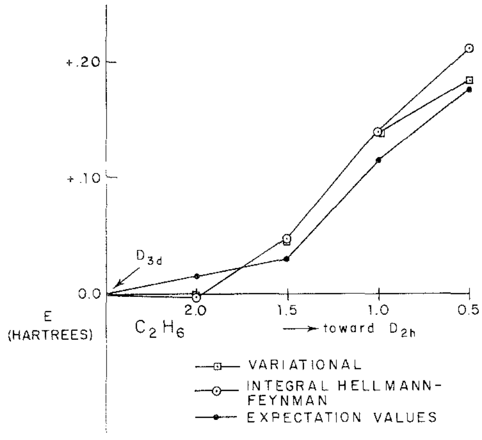

Fig. 2a. Potential curves (including nuclear repulsion) for C_2H_6 motion from D_{2h} "bridged" structure to D_{3d} equilibrium structure. Curves are constructed from expectation values (points), integral Hellmann-Feynman values of energy differences (circles), and variational estimates of energy differences (squares). The origin $E=0$ is the equilibrium D_{3d} structure. The three estimates are qualitatively consistent in this case

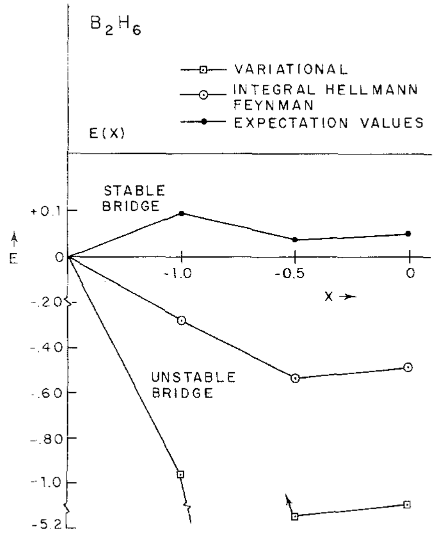

Fig. 2b. Potential curves for B_2H_6 motions computed in the three ways disagree drastically. Note a change of scale between $E>0$ and $E<0$, where $E=0$ refers to the D_{2h} bridged structure, and the discontinuity in the scale from -1 Hartree to -5 Hartrees

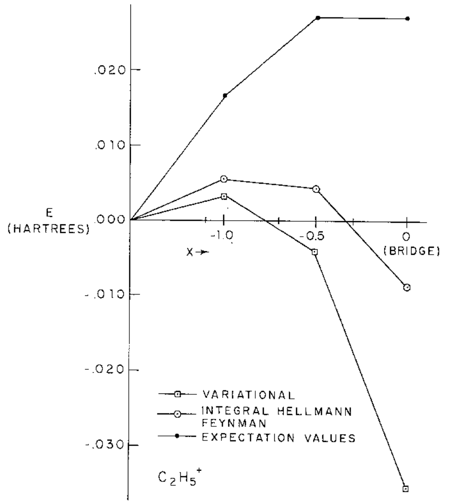

Fig. 2c. Integral Hellmann-Feynman and variational potential curves indicate that C_{2v} bridged $C_2H_5^+$ is the most stable geometry, in contradiction to expectation values. Note that the energy scale is different from that of Fig. 2a: the maximum error in variational estimates is 0.06 Hartrees, in integral Hellman-Feynman estimates, 0.04 Hartrees

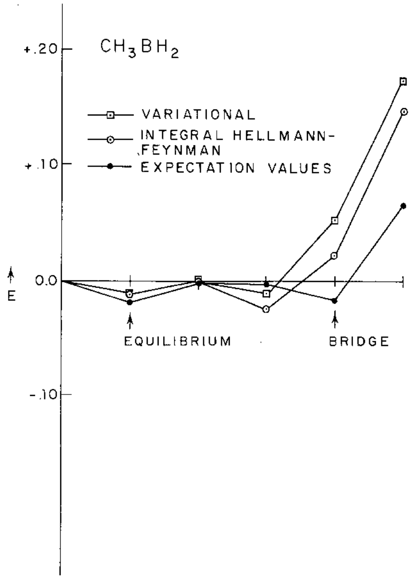

Fig. 2d. All three potential curves agree that there are stable open and bridge CH_3BH_2 geometries. However, integral Hellmann-Feynman and variational energy estimates predict a slightly different structure for the bridged species

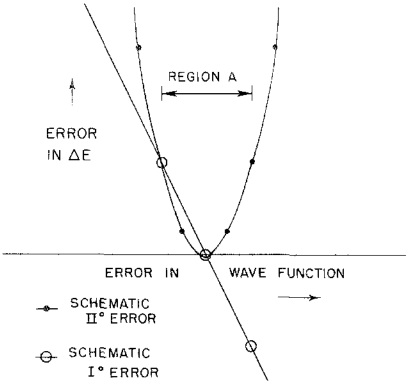

Fig. 3. Outside Region A, for serious errors in the wave functions of two species, a second order estimate of ΔE (points) can be worse than an estimate with first order errors (circles) if the second order errors of the latter estimate are small or tend to cancel the first order errors. We plot a straight line reflecting first order effects on ΔE computed with error in the wave function, and a parabola reflecting only second order effects on ΔE arising from wave function error. The lines intersect at two points. One corresponds to zero error in the wave function and zero error in ΔE. The other intersection corresponds to a second order error equal in value to the first order error; this intersection occurs for high curvature of the parabola. In the region A (small wave function error) the magnitude of ΔE error is less for the second order calculation than for the first order calculation. This is the situation we ordinarily think of when we contrast first and second order computations. However, outside region A the error in the second order value of ΔE exceeds the error of the first order value of ΔE. Thus the effort necessary to perform the second order computation is not always justified

of the reaction coordinates. The reaction in the ABH_5 systems is the transfer of hydrogen atom from A to B; the "reaction" in the A_2H_6 systems is the distortion from D_{3d} to a bridged D_{2h} structure. The reaction coordinate is the difference in the X-coordinate of the migrating hydrogen(s) and the X-coordinate of the spherical Gaussian representing the A–B sigma bond in the ABH_5 systems; in the A_2H_6 systems, the reaction coordinate is the X-coordinate of a potential bridge hydrogen.

From the figures and the tables, one gathers the impression that although there is a strong correlation between the several estimates of electronic energy changes (except for pathological cases in B_2H_6), errors in the potential curves are large due to the tendency of nuclear energy changes to cancel electronic energy changes. Although there is qualitative agreement in the CH_3BH_2 and CH_3CH_3 curves, there is a contradiction in the descriptions of the relative stability of bridged and open forms of $CH_3CH_2^+$. Further, most serious, the B_2H_6 curves produced by direct ΔE computations bear no resemblance to any reasonable energy curves.

When S_{0F} is near unity, the variational corrections are very small, as one might expect. However, one major feature of these computations is that (a) variational "corrections" are often large, particularly if S is small, and (b) even when variational corrections are comfortably small, the variationally corrected energy difference is not necessarily in closer agreement with expectation value differences than the simpler integral Hellmann-Feynman estimate. It is not impossible that the variationally determined estimates are "better" than expectation value differences in isolated cases. For example the barrier to internal rotation is estimated to be 6 kcal/mole by expectation value difference; the integral Hellmann-Feynman estimate is 13.5 kcal/mole, while the variational estimate is the best of the three, 2.6 kcal/mole [13]. However, the variational estimate can be far worse – ludicrously worse – than expectation value differences. In B_2H_6 the barrier to internal rotation is estimated as 0.0105 Hartrees by the integral-Hellmann-Feynman formula, 0.0135 by expectation value difference, and 0.285 by the variation method, more than an order of magnitude away from a reasonable estimate. This deterioration in a second order estimate relative to a first order estimate can be understood qualitatively by reference to the graph in Fig. 3. The utility of the variational correction depends on the magnitude of the slope in the Ω_{iHF}-wave function plot relative to the curvature in the $[\Delta\mathscr{H}]$-wave function plot. In certain cases the guarantee of first-order stability in $[\Delta\mathscr{H}]$ may carry with it an increase in curvature of the error plot. In Region A (Fig. 3), the variational correction is useful; outside A, the "correction" is of no use.

In this restricted application at least, the variational method shows no substantial advantage over the simplest integral Hellmann-Feynman formula. The problem may lie in the oversimplified choice of mixing only ψ_A with ψ_B in the variation, or may lie within the variation expression itself. The first restriction can be overcome at some computational expense, by increasing the flexibility of the variation. However, if the variationally stable expression does not provide the accuracy required, (the guarantee that energy errors are of second order in wave function errors does not imply that the errors are small) other expressions must be sought. To make a choice between these alternatives, substantial computation may be necessary. We are not inclined to pursue the test, since we have shown that given use of a common basis, the simple integral Hellmann-Feynman formula becomes quite accurate [7].

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References

1. Parr,R.G.: J. Chem. Phys. **40**, 3726 (1964); Kim,H., Parr,R.G.: J. Chem. Phys. **41**, 2892 (1964); see also Richardson,J.W., Pack,A.K.: J. Chem. Phys. **41**, 897 (1967)
2. Trindle,C.: J. Am. Chem. Soc. **92**, 3251, 3255 (1970); Shchembelov,G.A., Ustynyuk,Y.A.: J. Am. Chem. Soc. **96**, 4189 (1974)
3. Melrose,M.P., Parr,R.G.: Theoret. Chim. Acta (Berl.) **8**, 150 (1967)
4. Cooney,W.A.: Intern. J. Quantum Chem. **3**, 381 (1970)
5. Epstein,S., Hurley,A.C., Wyatt,R.E., Parr,R.G.: J. Chem. Phys. **47**, 1275 (1967)
6. Silverstone,H.J.: J. Chem. Phys. **43**, 4537 (1965)
7. Trindle,C., George,J.K.: Intern. J. Quantum Chem. (in press)
8. Marron,M.T., Weare,J.H., Intern. J. Quantum Chem. **2**, 729 (1968)
9. Frost,A.A.: J. Chem. Phys. **47**, 3707, 3714 (1967); for a more recent application, see Nelson,J.L., Frost,A.A.: Theoret. Chim. Acta (Berl.) **29**, 75 (1973)
10. King,H.F., Stanton,R.E., Kim,H., Wyatt,R.E., Parr,R.G.: J. Chem. Phys. **47**, 1936 (1967)
11. Edmiston,C., Lindner,P.: Intern. J. Quantum Chem. **7**, 309 (1973)
12. QCPE, Chemistry Department, Indiana Univ., Bloomington, Ind. 47001, Program 125
13. Compare Parr,R.G., Wyatt,R.E.: J. Chem. Phys. **44**, 1529 (1966)

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