

## The Integral Hellmann-Feynman Theorem Applied to Hydrogen Peroxide

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The integral Hellmann-Feynman (IHF) theorem developed by PARR [1—7] has raised hopes that the origin of barriers to internal rotation could be isolated by *ab-initio* calculations. The method is practicable for any molecule for which a wavefunction of reasonable quality is available. In such instances, the rotational barriers calculated by the IHF theorem ought to be comparable to or better than those obtained by the standard method of subtracting total SCF energies of the different conformations. To date, the successful application based on PITZER and LIPSCOMB's [8] ethane wavefunctions has provided an encouraging confirmation of the usefulness of the IHF approach [5, 6].

Very recently three sets of molecular orbital wavefunctions for the  $H_2O_2$  molecule have become available: the LCAO-MO-SCF-STO wave functions of KALDOR and SHAVITT [9], the LC(Double-Zeta)AO-MO-SCF functions with scaled hydrogens of FINK and ALLEN [10, 11] and the LCAO-MO-SCF functions of PALKE and PITZER [12] using exponents optimized for  $H_2O$ . Working independently, various workers have applied the IHF theorem to these wave functions: the first set has been treated by MELROSE and PARR [13], the second by FINK and ALLEN [14], and the third by the present authors. In each case the results for the *cis-trans* barrier are somewhat discouraging.

Within the framework of self-consistent-field theory and the Born-Oppenheimer approximation, the IHF theorem gives the *cis-trans* barrier to internal rotation ( $\Delta W_{IHF}$ ) as the sum of a nuclear-nuclear ( $\Delta V_{nn}$ ) and an electronic ( $\Delta E_{el}$ ) barrier. In particular

$$\Delta W_{IHF} = \Delta V_{nn} + 2 \sum_{ij} \frac{\langle \phi_i^{cis} | V_{ne}^{cis} - V_{ne}^{trans} | \phi_j^{trans} \rangle}{\langle \phi_i^{cis} | \phi_j^{trans} \rangle} \quad (1)$$

where  $\phi_i^x$  is the  $i^{\text{th}}$  MO for the  $x$  conformation. The double summation is diagonalized by a transformation of the wave functions to corresponding orbitals (CO),  $\hat{\phi}_i^x$ . The addition theorem for spherical harmonics is then applied to the difference of the nuclear-electronic operators, and the transition density is expanded in a Fourier series in  $\varphi$  [6]. The matrices  $U$  and  $V$  which transform the PALKE and PITZER MO's and CO overlaps are listed in Tabs. 1—3. These matrix elements are defined by

$$| \hat{\phi}_i^{cis} \rangle = \sum_j | \phi_j^{cis} \rangle \langle \phi_j^{cis} | \hat{\phi}_i^{cis} \rangle \equiv \sum_j | \phi_j^{cis} \rangle U_{ji} \quad (2)$$

Table 1.  $U$ -Matrix<sup>a</sup>

$\langle \phi_i^{cis}  $	$ \phi_j^{cis}\rangle$								
	$\hat{i} = 1$	2	3	4	5	6	7	8	9
$\langle 1a_1  $	.9372162	-.3414402	.0257790	-.0148274	.0000000	.0000000	-.0599231	-.0238535	.0005415
$\langle 2a_1  $	.2656205	.6857002	.2890288	-.0939969	.0000000	.0000000	.1678040	.5675361	-.1289673
$\langle 3a_1  $	.0108571	.0143741	.1352575	.7660073	.0000000	.0000000	-.0080941	-.1028787	-.6196485
$\langle 4a_1  $	-.0422920	-.2086820	-.7171441	.0958493	.0000000	.0000000	-.0594782	.6368394	-.1485881
$\langle 1a_2  $	.0000000	-.0000000	.0000000	-.0000000	.0017544	.9999985	-.0000000	-.0000000	-.0000000
$\langle 1b_1  $	.0000000	-.0000000	.0000000	-.0000000	.9999985	-.0017544	-.0000000	-.0000000	-.0000000
$\langle 1b_2  $	-.0142664	-.2124841	-.0247132	.0175498	.0000000	.0000000	.9765405	-.0098411	-.0000005
$\langle 2b_2  $	-.2208058	-.5657092	.5907978	-.1966554	.0000000	.0000000	-.1034189	.4379517	-.2024977
$\langle 3b_2  $	.0143654	.0655952	-.1831797	-.5966650	.0000000	.0000000	.0179168	-.2632239	-.7323382

<sup>a</sup> The coordinate system of PALKE and PRYZER was modified in the *cis*-conformation, so the hydrogen atoms lie in the  $y = 0$  plane.

Table 2.  $V$ -Matrix

$\langle \phi_i^{trans}  $	$ \phi_j^{trans}\rangle$								
	$\hat{i} = 1$	2	3	4	5	6	7	8	9
$\langle 1a_g  $	.9372142	-.3414528	.0257596	-.0147368	.0000000	.0000000	-.0599275	-.0238211	-.0001261
$\langle 2a_g  $	.2638659	.5844100	.2937684	-.1501219	.0000000	.0000000	.1684396	.5573098	.1189757
$\langle 3a_g  $	.0320099	.1194329	.4556174	.5700071	.0000000	.0000000	.0235383	-.3746704	.5579282
$\langle 4a_g  $	-.0291707	-.1662015	-.5683643	.3608175	.0000000	.0000000	-.0524990	.5263051	.4884114
$\langle 1a_u  $	-.0000000	.0000000	.0000000	-.0000000	.9999985	-.0017544	-.0000000	.0000000	.0000000
$\langle 1b_u  $	-.0000000	.0000000	.0000000	-.0000000	.0017544	.9999985	.0000000	.0000000	.0000000
$\langle 1b_u  $	-.0142781	-.2125114	-.0246710	.0175318	.0000000	.0000000	.9765356	-.0098391	.00007399
$\langle 2b_u  $	-.2230625	-.5686036	.5855637	-.2454816	.0000000	.0000000	-.1037211	.4192426	.1930404
$\langle 3b_u  $	.0129592	.0680783	-.1972763	-.6739971	.0000000	.0000000	.0186240	-.3091960	.6314666

Table 3. *Overlap Integrals*

$i$	1	2	3	4	5	6	7	8	9
$\langle \hat{\phi}_i^{\text{cis}}   \hat{\phi}_i^{\text{trans}} \rangle$	1.0000003	.9999985	.9922593	.9998183	.9999994	1.0000015	.9999992	.9999899	.8301348

Table 4. *Summary of Integral Hellmann-Feynman Calculations for cis-trans Barrier in H<sub>2</sub>O<sub>2</sub>*  
(All numbers in atomic units)

Wave function type	Author	$\Delta W_{\text{exp}} = .0112^a$		
		$\Delta V_{\text{HF}}$	$\Delta E_{\text{CI}}$	$\Delta W_{\text{SCF}}$
LC(Double-Zeta)AO-MO-SCF	FINK and ALLEN	.0938	-.0547	.0391
LCAO-MO-SCF-STO	MELROSE and PARR	.1123	-.0626	.0497
LCAO-MO-SCF-STO, H <sub>2</sub> O exponents	Present work	.1123	-.0603	.0520

<sup>a</sup> HUNT, R. H., R. A. LEACOCK, C. W. PETERS, and K. T. HECHT: J. chem. Physics **42**, 1931 (1965).

and

$$|\hat{\phi}_i^{\text{trans}}\rangle = \sum_j |\phi_j^{\text{trans}}\rangle \langle \phi_j^{\text{trans}} | \hat{\phi}_i^{\text{trans}}\rangle \equiv \sum_j |\phi_j^{\text{trans}}\rangle V_{ji}. \quad (3)$$

After Eq. (1) is diagonalized and the necessary integrations performed numerically\*, the electronic barrier is found to be  $-.0603$  au and the total barrier to internal rotation,  $.0520$  au. These results and those of other workers are summarized in Tab. 4, as are the barriers obtained by direct subtraction of total SCF energies ( $\Delta W_{\text{SCF}}$ ).

The rotation barrier as calculated from the wave functions of PALKE and PITZER is comparable to the results of FINK and ALLEN [14] and of MELROSE and PARR [13]. In each case the barrier is inferior to that obtained by the SCF subtraction method. Consequently the IHF theorem when applied to such wave functions can give no information on the barrier in  $\text{H}_2\text{O}_2$ . Recent calculations of FINK and ALLEN [14] lead to similar conclusions for a number of molecules.

Evidently, the IHF theorem must be modified in some way if it is to be applicable to wavefunctions of presently available quality.

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\* The integrations over  $r$  and  $\varphi$  are performed numerically by a  $10 \times 10$  Gaussian quadrature grid and the  $\varphi$  integration by a 10 point grid over each interval  $(-\pi/2m) \leq \varphi \leq (\pi/2m)$  and  $(n\pi/2m) \leq \varphi \leq [(n+2)\pi/2m]$ ,  $n$  odd, where  $m (= 1, 3, \dots)$  is the  $m$ -th order component of the transition density.

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