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Some Integral Hellmann-Feynman Calculations on Hydrogen Peroxide and Ammonia

M. P. MELROSE and ROBERT G. PARR

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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Barriers to internal rotation in H_2O_2 and to inversion in NH_3 are calculated by the Integral Hellmann-Feynman theorem. The results are compared with barriers found by the difference in expectation values and with the experimental results, and the agreement is found to be poor. Corresponding Orbitals are presented for the conformers considered.

Le théorème intégral d'Hellman-Feynman est utilisé pour calculer les barrières de rotation interne de H_2O_2 et d'inversion de NH_3. Les résultats sont comparés avec les barrières obtenues par différence entre valeurs moyennes et avec les résultats expérimentaux; l'accord est médiocre. Les orbitales correspondant aux conformations considérées sont présentées.

Mittels des integralen Hellmann-Feynman-Theorems wurden die Rotationsbarriere von H_2O_2 und die Inversionsbarriere von NH_3 berechnet. Die Ergebnisse werden mit den Ergebnissen direkter Energieberechnungen und experimentellen Daten verglichen. Die Übereinstimmung ist schlecht.

Introduction

Recently, KALDOR and SHAVITT [1, 2] have calculated LCAO SCF wavefunctions for H_2O_2 and NH_3. By taking the difference in expectation values (ΔW_{ed}) for various configurations these workers were able to estimate barriers to rotation and inversion. The Integral Hellmann-Feynman Theorem [3] provides an alternative method of computing these quantities (as ΔW_l) which at the same time gives physical insight into the problem through the idea of transition density. Agreement, or lack of it, between ΔW_{ed} and ΔW_l throws on the reliability of the wavefunctions when they are to be used to describe changes in molecular conformation. For, in the case of the exact wavefunction, ΔW_{ed} and ΔW_l are equal. There are circumstances [4] in which this is also true for the SCF wavefunction. In general, however, they will not be equal. The prime example [5] of close agreement between ΔW_{ed}, ΔW_l and the experimental value is the rotation barrier in ethane, where the LCAO SCF wavefunctions of PITZER and LIPSCOMB [6] were used. Indeed, the success of this calculation suggested that the rotation problem at least could be discussed without the complication of electron correlation.

Scheme of the Calculations

It has been shown elsewhere [3], that the electronic energy change for an isoelectronic process, such as a change in nuclear conformation $X \to Y$, may be written

$$\Delta E_l = \langle \Psi_X \mid \Delta V_{ne} \mid \Psi_Y \rangle / \langle \Psi_X \mid \Psi_Y \rangle \,. \tag{1}$$

In this formula ΔV_{ne} is the difference in nuclear attraction operators and Ψ_X and Ψ_Y are the electronic wavefunctions for the two conformers. The total energy change is then found by including the nuclear contribution ΔV_{nn}, so that the full Integral Hellmann-Feynman formula is

$$\Delta W_I = \Delta V_{nn} + \langle \Psi_X \mid \Delta V_{ne} \mid \Psi_Y \rangle / \langle \Psi_X \mid \Psi_Y \rangle \,. \tag{2}$$

In the case where Ψ_X and Ψ_Y are single determinants of MO's, ϕ_i^X and ϕ_i^Y, it is possible to transform to another basis ϕ_i^X and ϕ_i^Y, called the corresponding orbitals (CMO's), in which the right hand side of (1) has only diagonal matrix components:

$$\Delta E_I = 2 \sum_i \langle \phi_i^X \mid \Delta V_{ne} \mid \phi_i^Y \rangle / \langle \phi_i^X \mid \phi_i^Y \rangle \,. \tag{3}$$

Geometry and Orbitals

The CMO's quoted at the end of this paper refer to the original coordinate systems of Kaldor and Shavitt which are reproduced here for convenience.

Fig. 1 shows the coordinate system for H_2O_2. The available wavefunctions had been calculated with all bond lengths and the HOO angle kept constant. Thus, rotation was considered as a change in the dihedral angle χ only, from $\chi = 0$ (cis H_2O_2) to $\chi = 180°$ (trans H_2O_2).

The coordinate system for NH_3 is shown in Fig. 2. Inversion was considered as a change in the angle θ (between the NH bond and the symmetry axis) from $\theta = 90°$ (planar) to $\theta = 68°$ (pyramidal) — with the additional complication that the NH bond length was allowed to increase during the process. It was to be expected that this would make the problem more subtle than rotation.

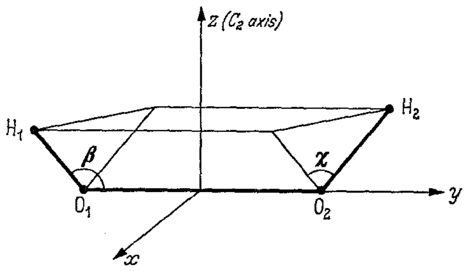

Fig. 1. Coordinate System for H_2O_2

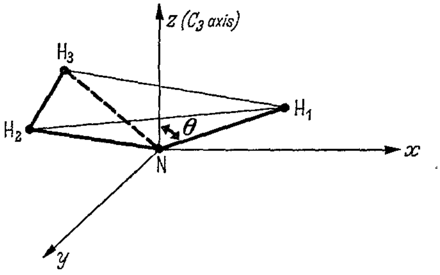

Fig. 2. Coordinate System for NH_3

In addition to calculating the MO's for NH_3 with a minimal basis set of 8 atomic orbitals (referred to as the MIN set) Kaldor and Shavitt also provided two extended basis set wavefunctions. One of these (the DN set) was a 13 orbital basis in which the nitrogen atom was allocated a 'double zeta' set of atomic orbitals. The other extended basis set (the MBO set) employed 12 atomic orbitals in which the valence orbitals on the nitrogen atom were augmented by functions having maxima in the NH bond regions.

Integrals

The evaluation of ΔE_I by Eq. (3) required the calculation of two and three centre nuclear attraction integral and overlap integrals over basic atomic orbitals. The three centre integrals were computed by the method of Magnusson and Zauli [7] (3 dimensional quadrature in a 7500 point net) and the two centre integrals were evaluated analytically. Then it only remained to obtain the coefficients of the Corresponding Orbitals. The matrix operations whereby these may be obtained from MO coefficients have already been given by Wyatt and Parr [5].

Results and Discussion

H_2O_2

The results are conveniently summarised in Tab. 1, where the values of ΔW_{ed} are included for comparison. The complete results (KALDOR and SHAVITT considered six conformations) for ΔW_{ed} gave a minimum in the potential energy curve at $\chi = 120°$, indicating two barriers: 11.8 kcal/mole through the cis position and 2.2 kcal/mole through the trans. (The experimental barriers, as quoted in Ref. [1], are 7.0 and 1.1 kcals respectively).

Table 1 *(atomic units)*

	ΔE_l	ΔV_{nn}	ΔW_l	ΔW_{ed}
0° → 120° Rotation	−0.0651	0.0952	0.0301	0.0190
0° → 180° Rotation	−0.0626	0.1123	0.0497	0.0153

The magnitudes of ΔW_l are respectively one and a half and three times greater than those of ΔW_{ed}; and they also suggest that there is no minimum at all between the cis and trans positions. The Hellmann-Feynman calculation would thus give only one barrier, of 0.0497 au or about 30 kcals. It would appear that simple energy differences give better results than the Hellmann-Feynman theorem for these wavefunctions. However, the Hellmann-Feynman result can be regarded as a comment on the reliability of these wavefunctions as far as the rotation problem is concerned; because the good agreement between ΔW_{ed} and experiment is not maintained by a better variational function [8]. FINK and ALLEN [8] have also failed to locate a minimum between the cis and the trans conformations, and their (Double-zeta) wavefunctions are believed to be quite close to the Hartree Fock limit. The ΔW_{ed} value obtained for the cis → trans rotation is 0.02633 au or 16.53 kcal/mole. Hellmann-Feynman calculations [9] on the same wavefunctions give 0.03912 au or 24.55 kcal/mole, roughly the same as in the present work.

NH_3

The calculated energy values are conveniently summarised in Tab. 2. The experimental value of the barrier is 0.25 eV or 0.0093 au (as quoted in Ref. [2]).

Table 2

	MIN $(\theta = 68°)$ experimental equilibrium conf.	MIN $(\theta = 65°)$ calc. min. energy conf.	DN $(\theta = 68°)$	MBO $(\theta = 68°)$
ΔE_l	−0.20096	−0.24203	−0.12563	0.00165
ΔV_{nn}	0.17905	0.21659	0.11890	0.01829
ΔW_l	−0.02190	−0.02544	−0.00673	0.01994
ΔW_{ed}	0.01673	0.01843	−0.00341	0.0000

Table 3. H_2O_2 *Corresponding Orbitals for 0° to 120° Rotation*

CMO pair	Contribution to ΔE_l (au)	Overlap Integral $\langle\phi_i^X \mid \phi_i^Y\rangle$	Coefficients[a]					
			$O_1 1s$	$O_1 2s$	$O_1 2p_x$	$O_1 2p_y$	$O_1 2p_z$	$H_1 1s$
1a	+0.00239	1.00000	0.43655 0.43656	0.33301 0.33298	−0.06747 −0.06749	−0.34009 −0.34009	−0.11168 −0.11170	0.00004 0.00009
2a	−0.00864	1.000	−0.06054 −0.06054	0.43543 0.43542	0.03131 0.03128	0.41823 0.41823	0.06817 0.06818	0.00009 0.00012
3a	−0.02222	0.93621	0.00390 0.00380	0.10166 0.10376	−0.32467 −0.21750	0.15560 0.15777	−0.38784 −0.46971	−0.32493 −0.33006
4a	+0.00240	0.99999	0.57613 0.57613	−0.39625 −0.39624	0.07425 0.07492	0.31209 0.31209	0.11899 0.11899	−0.00008 −0.00011
5a	+0.01571	0.89389	0.01565 −0.01720	−0.10972 0.14690	−0.64951 −0.51714	0.01338 −0.02659	0.22236 0.41861	0.16241 −0.24229
1b	−0.00002	1.00000	0.72003 0.72003	−0.07266 −0.07268	0.01039 0.01037	0.01331 0.01328	0.01697 0.01697	0.00002 0.00005
2b	+0.00342	0.99993	−0.09868 −0.09869	0.74760 0.74768	−0.06692 −0.06692	−0.10253 −0.10242	−0.10460 −0.10458	0.00008 0.00001
3b	+0.14898	0.92628	0.02012 0.00005	−0.08064 0.08439	−0.67833 −0.51419	0.01433 −0.03502	0.04418 0.16249	0.03205 −0.33921
4b	−0.17460	0.91396	−0.00958 −0.02386	−0.08635 0.03247	0.04530 −0.03002	0.06011 0.02992	0.50294 0.67320	0.48010 0.21229

[a] Coefficients of the other AO's can be obtained by symmetry.

The integral Hellmann-Feynmann result gives negative „barriers" for all sets except the MBO, where the sign is right but the magnitude is about twice the observed. In the MIN calculations, the experimental equilibrium configuration ($\theta = 68°$) is found to be more stable than the configuration with $\theta = 65°$, which

Table 4. H_2O_2 *Corresponding Orbitals for 0° (cis) → 180° (trans) Rotation*

CMO pair	Contribution to ΔE_l (au)	Overlap Integral	Coefficients[a]					
			$O_1 1s$	$O_1 2s$	$O_1 2p_x$	$O_1 2p_y$	$O_1 2p_z$	$H_1 1s$
1*a*	+0.00009	0.99999	0.72051	−0.07418	0.01242	−0.00730	0.01098	−0.00001
			0.72051	−0.07418	0.01243	−0.00730	0.01097	−0.00001
2*a*	−0.01716	1.000	−0.05006	0.44504	0.04870	0.40717	0.06456	0.00005
			−0.05006	0.44504	0.04869	0.40717	0.06458	0.00006
3*a*	+0.04350	0.85605	0.02048	−0.14736	−0.56940	0.02024	0.30165	0.22002
			−0.02116	0.18214	−0.39523	−0.02510	0.45223	−0.30485
4*a*	−0.04298	0.92125	−0.01124	−0.06366	0.43344	−0.18278	0.33131	0.28905
			−0.01166	−0.06115	0.31270	−0.18557	0.48154	0.28633
5*a*	+0.01406	0.99999	0.06507	−0.50055	0.15397	0.46121	0.16154	−0.00006
			0.06507	−0.50051	0.15402	0.46120	0.16153	−0.00014
1*b*	−0.00006	0.99999	0.69762	0.03831	0.00080	−0.00195	0.00137	0.00003
			0.69762	0.03832	0.00079	−0.00197	0.00138	0.00002
2*b*	+0.01025	0.99993	−0.20208	0.74436	−0.10778	−0.10255	−0.10489	0.00033
			−0.20226	0.74543	−0.10770	−0.10025	−0.10479	−0.00017
3*b*	+0.09494	0.92432	0.03228	−0.05081	−0.56888	−0.01897	−0.25724	−0.25871
			0.02805	−0.01698	−0.39675	−0.02762	−0.36296	−0.33223
4*b*	−0.13396	0.88621	0.01097	−0.14143	−0.36267	0.06023	0.43468	0.40570
			−0.01904	0.11431	−0.24690	−0.03263	0.62896	−0.19175

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[a] Coefficients of the other AO's may be found by symmetry.

had the *lowest* energy in the variational calculation. There is little agreement between ΔW_l and ΔW_{ed}. They are closest for the DN set, which happens to be the best variational calculation. Also there is little or no regularity (as between different basis sets) in the contributions to ΔE_l from each CMO.

Table 5. *Corresponding Orbitals for* NH_3 *with minimal basis set*

CMO pair	Contribution to ΔE_l (au)	Overlap Integral	Coefficients[a] N1s	N2s	N2p_x	N2p_x	$H_1$1s
1. Inversion from the planar (θ = 90°, R_{NH} = 1.916 au) to the expt. equilibrium configuration (θ = 68°, R_{NH} = 1.957 au)							
$1a_1$	−0.03331	1.000	1.00174	−0.00209	0.0	−0.02205	−0.00929
			1.00128	0.00168	0.0	−0.01638	−0.01178
$2a_1$	−0.05923	0.98737	−0.18298	0.74487	0.0	−0.06520	0.16352
			−0.19498	0.83971	0.0	−0.11815	0.11181
$3a_1$	+0.05843	0.97589	0.01018	0.04863	0.0	0.99763	0.01048
			0.04634	−0.22170	0.0	0.89562	0.16210
e_x	−0.03318	0.96175	0.0	0.0	0.58443	0.0	0.48646
			0.0	0.0	0.59143	0.0	0.50192
2. Inversion from planar (θ = 90°, R_{NH} = 1.916 au) to minimum energy pyramidal configuration (θ = 65°, R_{NH} = 1.967 au)							
$1a_1$	−0.04047	0.99999	0.99494	0.02424	0.0	0.00193	−0.00351
			0.99493	0.02412	0.0	0.00383	−0.00353
$2a_1$	+0.00541	0.98931	−0.21628	0.74241	0.0	0.09888	0.16328
			−0.22414	0.80769	0.0	0.02708	0.13092
$3a_1$	−0.00489	0.96864	0.01957	−0.07382	0.0	0.99510	−0.01622
			0.06190	−0.38927	0.0	0.87524	0.16405
e_x	−0.04053	0.95270	0.0	0.0	0.58443	0.0	0.48646
			0.0	0.0	0.59226	0.0	0.50884

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[a] Coefficients of the other atomic orbitals, and of the CMO e_y, may be found by symmetry.

Table 6. *Corresponding Orbitals for* NH_3*, with the* DN *Basis Set*

Planar geometry: R_{NH} = 1.88029 au, θ = 90°; Pyramidal geometry: R_{NH} = 1.91033 au, θ = 68°

CMO pair	Contribution to ΔE_l (au)	Overlap Integral	Coefficients[a] N1s_1	N1s_2	N2s_1	N2s_2	N2p_{z_1}	N2p_{z_2}	$H_1$1s
$1a_1$	−0.01383	1.000	0.63818	0.17994	0.17331	0.15606	0.04548	0.01642	0.06502
			0.61311	0.20283	0.18398	0.16310	0.01210	0.01638	0.05800
$2a_1$	+0.05591	0.98819	−0.63710	0.00247	0.40006	0.34101	0.17293	0.06244	0.14786
			−0.63057	−0.01112	0.39722	0.36071	0.09587	0.05619	0.14216
$3a_1$	−0.04952	0.99191	0.10666	−0.01132	−0.10129	−0.08683	0.76087	0.24773	−0.03749
			0.12570	−0.00884	−0.31241	−0.12774	0.69103	0.28227	0.09611
							N2p_{x_1}	N2p_{x_2}	$H_1$1s
e_x	−0.02769	0.97287					0.43249	0.25508	0.41969
							0.41678	0.26667	0.44779

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[a] Coefficients of the other atomic orbitals, and of the CMO e_y, may be found by symmetry.

Table 7. *Corresponding Orbitals for* MBO *Basis Set*

(Planar Geometry: $R_{NH} = 1.90267$ au, $\theta = 90°$; Pyramidal Geometry: $R_{NH} = 1.91113$ au, $\theta = 68°$)

CMO pair	Contribution to ΔE_l (au)	Overlap Integral	Coefficients[a]					
			N1s	N2s	N2s_B	N2p_z	N2p_{zB}	$H_1$1s
$1a_1$	−0.00568	1.0000	0.97628	0.08105	−0.01084	0.01471	0.00676	0.00942
			0.97630	0.08091	−0.01062	0.01493	−0.00032	0.00948
$2a_1$	+0.05077	0.99480	−0.29315	0.77044	−0.09765	0.11453	0.05261	0.18102
			−0.29545	0.78553	−0.10162	0.09750	−0.05498	0.17641
$3a_1$	−0.00753	0.99096	0.02594	−0.12074	0.01531	0.74075	0.34027	−0.02818
			0.04630	−0.29705	−0.07039	0.71297	0.28634	0.10562
						N2p_x	N2p_{xB}	$H_1$1s
e_x	−0.01837	0.96952				0.62068	0.00604	0.44738
						0.61707	0.01176	0.46756

[a] Coefficients of the other atomic orbitals, and of the CMO e_y, may be found by symmetry.

From this work and the results of other investigations* it is clear that available wavefunctions for ammonia are not good enough for the calculation of the magnitude (much less a discussion of the origin) of the inversion barrier. It is not even certain that the Hartree-Fock wavefunction, when it is available, will be adequate.

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* Mr. B. F. GRAHAM informs us that in Integral Hellmann-Feynman calculations using one centre LCAO SCF wavefunctions he obtained a barrier of 0.0275 au for MOCCIA's wavefunction and barriers of 0.0463 au and 0.0721 au for the wavefunctions (first and second 'build up') of JOSHI.

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Dr. M. P. MELROSE
Department of Chemistry
University of London
King's College
Strand, W.C. 2
London, England