

The balance between electronic and nuclear energy in conformational change

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The relative contributions of nuclear repulsion and electronic attraction to conformational rotational potentials have been analysed for several types of systems. It is shown that decomposition of a computed total energy into these two components provides a diagnostic tool for the evaluation of the reliability of such computations. It is also pointed out that Hartree-Fock theory is sufficient to reproduce experimental stereochemical observations, provided that one is aware of the accuracy needed to compute the molecular electronic wavefunction. This accuracy is predetermined by the nuclear or electronic dominance of the process.

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On a analysé les contributions relatives de la répulsion nucléaire et de l'attraction électronique par rapport au potentiel rotationnel conformationnel de plusieurs types de systèmes. On a montré que la décomposition, dans ces deux composantes, de l'énergie totale calculée fournit un outil diagnostique pour l'évaluation de la certitude de tels calculs. On met aussi en relief que la théorie de Hartree-Fock est suffisante pour reproduire des observations stéréochimiques expérimentales à condition que l'on soit conscient de la précision nécessaire pour calculer les fonctions d'onde électroniques moléculaires. Cette précision est prédéterminée par la dominance nucléaire ou électronique du processus.

[Traduit par le journal]

Introduction

With the advent and availability of computer programmes for the computation of the total energies and stable geometries of molecules, theoretical stereochemistry has entered an extremely productive era (1). Accumulated experience in this field seems to indicate that there are two classes of problems. In the first, it is found that SCF-MO computations performed at almost any level of accuracy afford fairly good agreement with experiment; but in the second, very extensive computations combined with careful geometry optimization are required to yield such agreement.

The classical example of the first type is rotation in ethane (2), and for the second type, the classical examples are rotation in hydrogen peroxide (3) and pyramidal inversion in ammonia (4). Thus, even the simplest semi-empirical computations are able to reproduce the *ca.* 3 kcal/mol barrier of ethane, but to reproduce the *trans* barrier to rotation in hydrogen per-

oxide (*ca.* 1 kcal/mol), it has been necessary to go almost to the Hartree-Fock limit using *d*-orbitals on oxygen and *p*-orbitals on hydrogen, in conjunction with geometry optimization at each torsional angle (3a).

It might be tempting to suggest that the difficulty lies in the relatively low barrier that is being computed. However, the rotational barrier in methanol is also about 1 kcal/mol, and it can be reproduced without great difficulty (5) (*i.e.*, methanol is a member of the first class of molecules). Consequently, it is clear that, for the class of compounds exemplified by H₂O₂, one has to use a much more accurate wavefunction than for the class of compounds exemplified by ethane.

Why it is necessary to approach the Hartree-Fock limit more closely in one case than in another does not appear to have been discussed previously, and the purpose of the present work is to attempt an analysis of this problem. In terms of this analysis it becomes possible, in

principle, to estimate the quality of computation that will be necessary to reproduce a particular observation.

Theory

In the Born-Oppenheimer approximation, the total energy (E_{tot}) of a molecular system is the sum of electronic attraction ($E_{\text{elec}} = T + V_{\text{ne}} + V_{\text{ee}}$, where T , V_{ne} , and V_{ee} are the kinetic energy, electron-nuclear attraction, and electron-electron repulsion terms, respectively), a negative quantity and nuclear repulsion (E_{nuc}), a positive quantity (eq. 1).

$$[1] \quad E_{\text{tot}} = E_{\text{elec}} + E_{\text{nuc}}$$

The nuclear repulsion component can be computed without difficulty, according to classical electrostatics, from the nuclear charges (Z_I , Z_J , etc.) and their interatomic distances (R_{IJ}) (eq. 2)

$$[2] \quad E_{\text{nuc}} = \sum_{I=1} \sum_{J>I} \frac{Z_I Z_J}{R_{IJ}}$$

In contrast, computation of the electronic component requires solution of the Schrödinger equation through the variation theorem (eq. 3).

$$[3] \quad E_{\text{elec}} = \frac{\langle \Psi_{\text{elec}} | H_{\text{elec}} | \Psi_{\text{elec}} \rangle}{\langle \Psi_{\text{elec}} | \Psi_{\text{elec}} \rangle}$$

Clearly, the effort required to evaluate eq. 2 is insignificant in comparison to what is needed for eq. 3.

It is therefore useful to be aware of the equality shown in eq. 1, because it means (1a) that a semi-quantitative understanding of E_{tot} based on experimental observations (e.g., observations of conformational equilibria) can be combined with a computation of E_{nuc} to provide a semi-quantitative understanding of E_{elec} and, in particular, its phase.¹

Our chemical experience is that molecules have stability with respect to separated atoms. This requires that E_{nuc} and E_{elec} always have opposite phase (see Fig. 1b). Were this not the case, our chemical experience would consist either of a collapsing universe (Fig. 1a) in which only a single giant atom exists, or a dissociating universe (Fig. 1c), in which only separated atoms

¹By phase we mean the direction of change, i.e. the sign of the derivative with respect to a geometrical parameter of the molecule.

exist. These alternatives are illustrated schematically for the general case of a diatomic molecule in Fig. 1, and they allow the formulation of a rule:

"The nuclear and electronic components of a molecular conformational potential curve always have opposite phase".

We may now note that, in any region of a potential curve corresponding to that cross-section of a conformational hypersurface which describes the conformational change, the total energy is in phase either with the electronic component or with the nuclear component. Employing the example of the stretching potential shown in Fig. 1b, it can be seen that at a large internuclear separation ($r_e < r < \infty$) the total energy is in phase with the electronic component (and may be said to be electronic dominant) and, at a shorter bond length ($0 < r < r_e$), the total energy is in phase with the nuclear component (and may be said to be nuclear dominant). This observation permits the formulation of a second rule:

"In any region of a potential curve, the variation of the total energy of a molecular system during conformational change is in phase either with the nuclear repulsion (nuclear dominant) or with the electronic attraction (electronic dominant)".

As a consequence of this second rule, we should recognize that the total energy may be in phase with one of these components throughout the conformational change, as in the case of rigid rotation in ethane in which the total

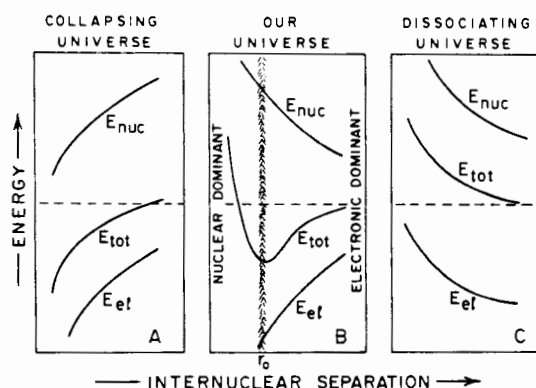


FIG. 1. Alternatives of nuclear and electronic components of the total energy. (A) Collapsing universe, where E_{nuc} and E_{elec} are in phase. (B) Our universe, where E_{nuc} and E_{elec} are in opposite phase. (C) Dissociating universe, where E_{nuc} and E_{elec} are in phase.

energy is in phase with the nuclear repulsion (see below), or there may be a cross-over from electronic dominance to nuclear dominance at some point. This cross-over represents a balance between the attractive electronic forces and the repulsive nuclear forces. These considerations permit the formulation of a third rule:

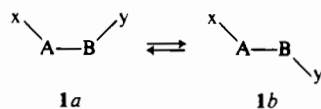
"Whenever there is a change from nuclear dominance to electronic dominance in a conformational process, this change will be found at an energy extremum".

Discussion

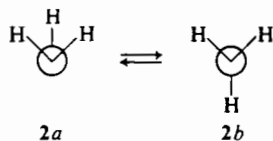
The preceding considerations have been derived by inductive reasoning, and we may now consider their application to the problems of torsion and pyramidal inversion.

(a) Rotation (Torsion)

In the general molecule 1, nuclear repulsion is a maximum and electronic attraction is a minimum in the most crowded conformation 1a if we allow rigid rotation only. The opposite is true for the less crowded conformation 1b.



Whether the actual structure adopted by 1 is closer to 1a or to 1b will then depend on the relative importance of nuclear repulsion and electronic attraction. For example, $\text{^-CH}_2\text{OH}$ (6) displays two energy minima corresponding to the W and Y conformations 2a and 2b.



As shown in Fig. 2, (i) the nuclear and electronic components have opposite phase; (ii) the total energy is in phase either with the nuclear repulsion or the electronic attraction; (iii) the more stable Y conformation is dominated by nuclear repulsion, and the less stable W conformation is dominated by electronic attraction; a balance between the two components is achieved at the transition state which connects the two minima. Thus, the rotational behaviour of $\text{^-CH}_2\text{OH}$ illustrates the operation of all three rules.

A second example is given in Fig. 3 for

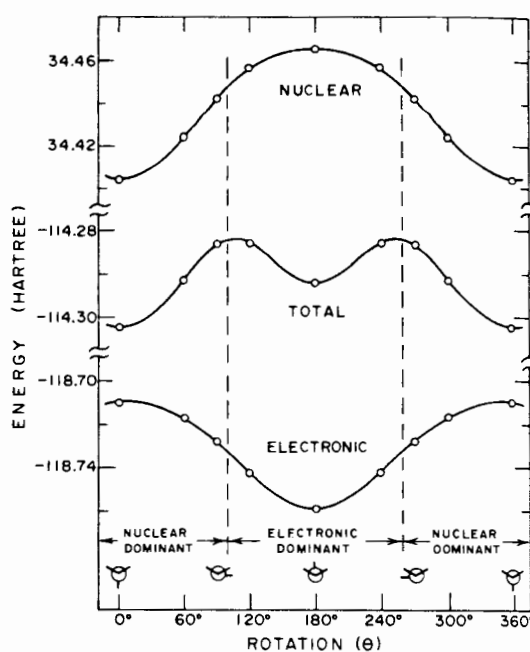


FIG. 2. The variation of total energy as well as its nuclear and electronic components of $\text{^-CH}_2\text{OH}$ with the rotational (dihedral) angle along the C—O bond.

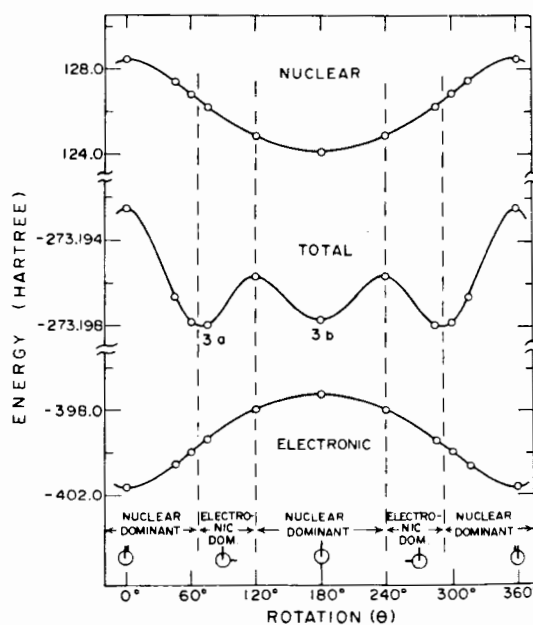


FIG. 3. The variation of total energy as well as its nuclear and electronic components of $\text{FCH}_2\text{—CH}_2\text{F}$ with the rotational (dihedral) angle along the C—C bond.

1,2-difluoroethane (STO-3G) (the higher nuclear repulsion component (3a).

Consequently, the low accuracy of the electronic component of hydrogen from that of the total energy component, the behavior to electronic rigid rotation (cf. Fig. 8), always dominates the relatively component the two m

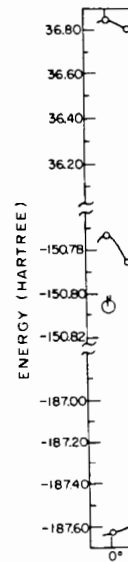
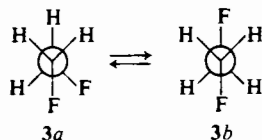


FIG. 4. The electronic energy component of the total energy with rotation angle.

1,2-difluoroethane as obtained by a minimal (STO-3G (7)) basis set calculation. In this case, the higher minimum (3b) is fully dominated by nuclear repulsion, and the change in dominance between the opposing nuclear and electronic components occurs in the *gauche* conformation (3a).



Consequently, both the position and the energy of the lower minimum (3a) depend upon the accuracy of the computation of the electronic component. The situation is analogous to that of hydrogen peroxide (*cf.* Fig. 4B) but different from that of ethane (*cf.* Fig. 5). In the latter case, the total energy is in phase with only one of the components. However, it should be noted that the behavior changes from nuclear dominance to electronic dominance as one changes from rigid rotation (*cf.* Fig. 5A) to relaxed rotation (*cf.* Fig. 5B) on the conformational hypersurface (8, 9). Because one of the components is always dominant the total barrier is always relatively easy to obtain even though the component barrier heights differ significantly in the two modes shown in Fig. 5 A and B.

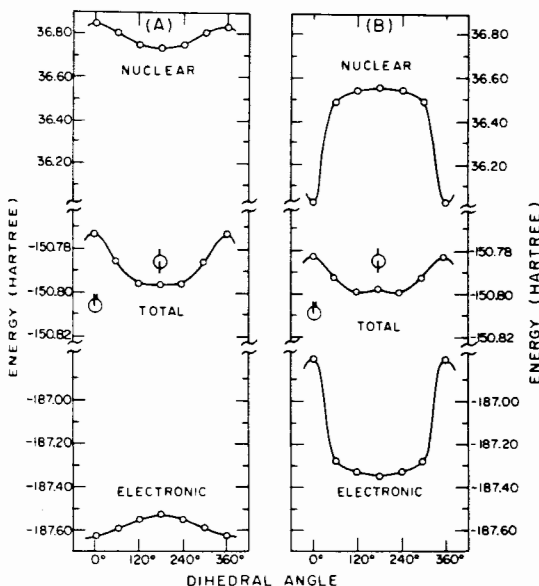


FIG. 4. The variation of nuclear repulsion, total and electronic energy of HOOH with angle of (A) rigid rotation and (B) relaxed rotation about the O—O bond.

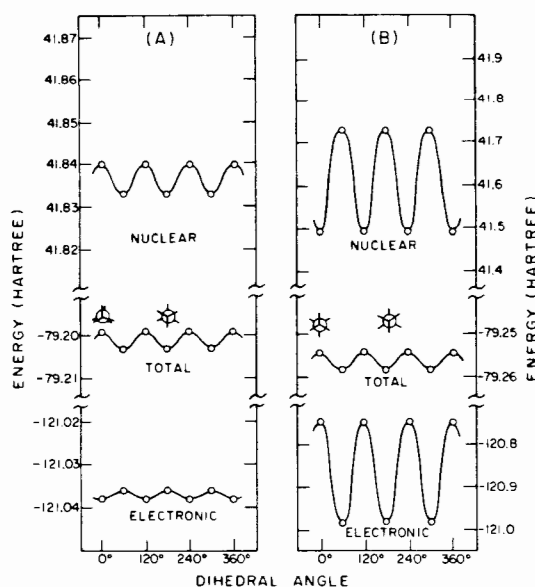
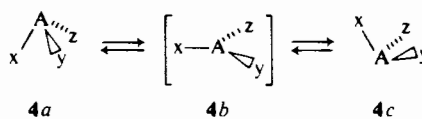


FIG. 5. The variation of nuclear repulsion, total and electronic energy of CH_3CH_3 with angle of (A) rigid rotation and (B) relaxed rotation about the C—C bond.

The situation is much more complicated in the case of H_2O_2 because there is a change from exclusive nuclear dominance to balanced dominance as one goes from Fig. 4A to Fig. 4B. Consequently, both geometry optimization (*i.e.*, relaxation) and the inclusion of polarization functions in the basis set are required to obtain the small *trans* barrier (Fig. 4B) (10).

(b) Inversion

In a pyramidal molecule 4,



nuclear repulsion is greater in the pyramidal conformations 4a and 4c than in the planar conformation 4b when rigid inversion (*i.e.*, inversion with fixed bond lengths) is considered. For relaxed inversion (*i.e.*, inversion with variable bond lengths) the opposite may be true. However, the barrier to pyramidal inversion is always dominated by one of the components and the minimum is always characterized by a change in dominance. Therefore, the computation of the barrier to inversion will depend upon the accuracy of the electronic component. The pyramidal inversion of NH_3 exemplifies this mode of motion (11).

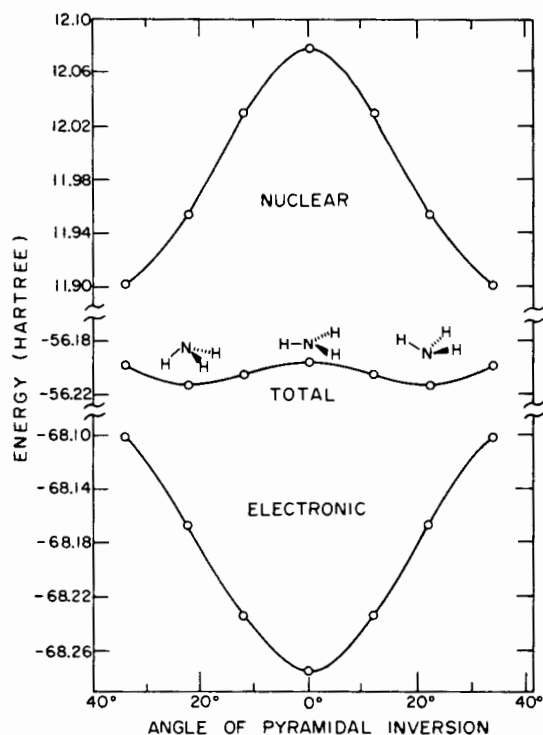
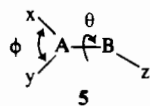


FIG. 6. The variation of nuclear repulsion, total and electronic energy of NH_3 with angle of relaxed pyramidal inversion.

Figure 6 shows relaxed pyramidal inversion of NH_3 . The total energy is nuclear dominant between the two minima, including the planar transition state. The minima are characterized by a change from nuclear to electronic dominance. The calculated barrier is thus very sensitive to the accuracy of the calculation.

(c) Rotation-Inversion

The conformational surface $E = E(\theta, \phi)$ associated with two independent modes of motion such as pyramidal inversion (ϕ) and rotation (θ) may be calculated for any molecule (e.g., **5**) that has these internal modes of motion available by virtue of its molecular structure



Two systems of interest are CH_2NO_2 (**6**) and NH_2PH_2 (**7**)

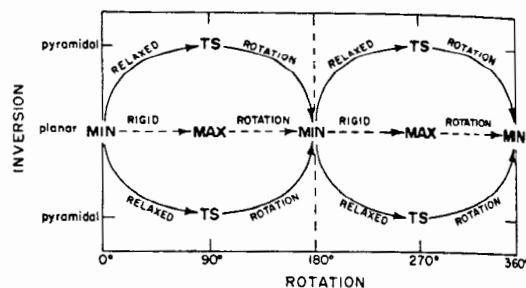
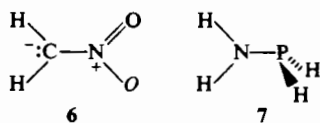


FIG. 7. The topological features of a general rotation-inversion surface.

The rotation-inversion surfaces of **6** (12) and **7** (13) are to be published elsewhere. However, Fig. 7 summarizes the topological features of both surfaces.

Rigid and relaxed rotational cross-sections of the surfaces of **6** and **7** are shown in Figs. 8 and 9 respectively. In the case of **6** the components are well behaved, and there is no change in dominance on going from rigid rotation to relaxed rotation. However, the situation with H_2NPH_2 is different. For the rigid rotation, the nuclear and electronic components are in phase with each other and with the total energy! This represents an exception to the three rules proposed above. However, when the geometry is relaxed to permit rotation and nitrogen inversion to occur simultaneously, the apparent

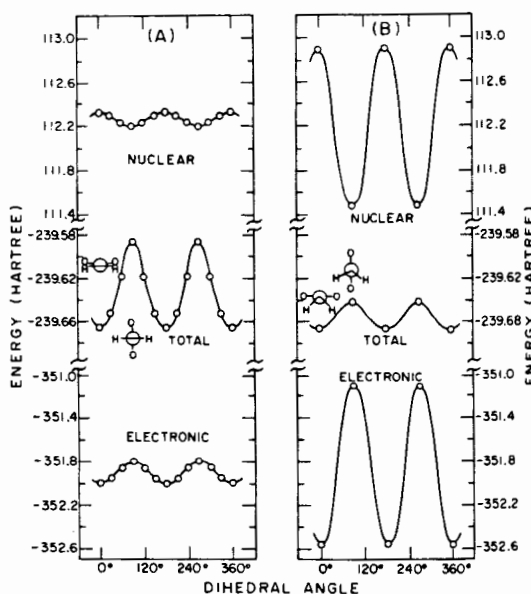


FIG. 8. The variation of nuclear repulsion, total and electronic energy of CH_2NO_2 with angle of (A) rigid rotation and (B) relaxed rotation about the C-N bond.

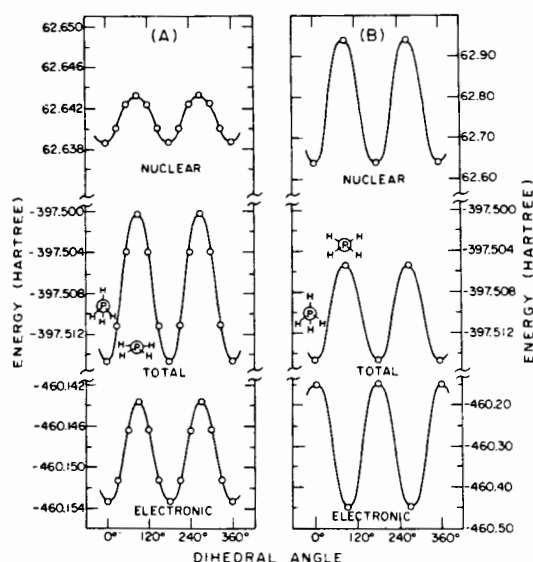


FIG. 9. The variation of nuclear repulsion, total and electronic energy of H_2PNH_2 with angle of (A) rigid rotation and (B) relaxed rotation about the P—N bond.

discrepancy disappears. This leads to the conclusion that the three rules are strictly valid along the "reaction coordinates". The rules may not be operative along an unstable cross-section, because the system will "roll down" from the side of the surface to the nearest minimum path.

Conclusion

In conclusion, it appears that when there is exclusive dominance of one component (either electronic or nuclear) it is relatively easy to reproduce the experimental stabilities (thermodynamic or kinetic) by theoretical calculations. However, when there is a change in dominance along a given mode of motion the accuracy of the calculations required to reproduce the corresponding experimental stabilities is very high.

Finally, it appears that the anti-parallelism of the phases of the nuclear and electronic components may be valid throughout the hypersurface or for only certain regions of it: the latter type of surface is the more intriguing. In this case, one of the two components may be in phase with the total energy in one region of the hypersurface, and the other component may be in phase with the total energy in another region of the hypersurface, as in the case of rigid and relaxed rotation. On going from one region of the hypersurface to the other, both the nuclear and the electronic components must change phase.

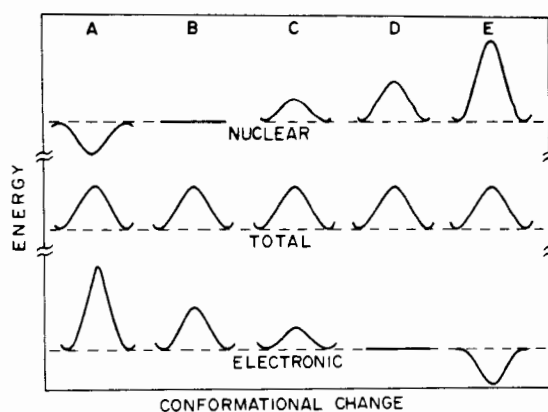


FIG. 10. The variation of the nuclear repulsion, total and electronic energy of a molecule with conformational change showing in five stages (A to E) the change in the phase of the two components but no change in the phase of the total energy.

Such a simultaneous change would require the existence of an intermediate region in which both components are in phase with the total energy. This is illustrated schematically in Fig. 10. Clearly, the situation is more complicated when there is a change of dominance during the conformational change, as in HO—OH , $\text{CH}_2\text{—OH}$, $\text{FCH}_2\text{—CH}_2\text{F}$, and NH_3 .

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