Theoret. Chim. Acta (Berl.) 63, 83–101 (1983)

THEORETICA CHIMICA ACTA

A Simple Perturbational Approach for the Determination of Favourable Reaction Pathways

Vinzenz Bachler

Max-Planck-Institut für Strahlenchemie, Stiftstraße 34–36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

E. Amitai Halevi

Technion–Israel Institute of Technology, Department of Chemistry, Technion City, Haifa 32000, Israel

A simple perturbational approach has been used to establish the symmetry conditions for energetically favourable nuclear motions on a potential energy surface. In particular, the operational rules of Orbital Correspondence Analysis in Maximum Symmetry (OCAMS) for specifying the symmetry species of the nuclear displacements, which make a symmetry forbidden pathway symmetry-allowed, have been derived. A general, symmetry-independent, procedure is then proposed for finding the energetically most favourable pathway by referring to the form of the overlap density function of non-correlating orbitals. The method is demonstrated by selecting from among the several symmetry-allowed nuclear motions on the potential energy surface for the H_2+D_2 exchange reaction, that which is energetically most favourable.

Key words: Orbital symmetry – Potential energy surface.

1. Introduction

Correlation diagram techniques and symmetry arguments are important for the rationalization of chemical reactivity [1] and the geometry of molecules in ground and excited states [2]. Orbital Correspondence Analysis in Maximum Symmetry (OCAMS) [3, 4] is a correlation diagram technique which employs symmetry efficiently. In this procedure, the largest common point group of reactants and products is retained along an adopted nuclear pathway and a correlation diagram between the wavefunctions of reactants and products is constructed. If the adopted path turns out to be symmetry-forbidden, OCAMS predicts how the symmetry of the pathway must be reduced in order to make it symmetry-allowed [3, 4]. Thus, information about the nature of the non-correlation is used to find those nuclear motions along which the wavefunctions of reactants and products remain in correlation.

The operational rules of OCAMS have been derived, using time-dependent perturbation theory [4]. In this paper we demonstrate how the operational rules of OCAMS follow from the requirement that nuclear displacements on a potential energy surface be energetically favourable. In addition, we propose a procedure for finding favourable pathways, which does not employ symmetry arguments but uses instead the information contained in the forms of non-correlating orbitals. This procedure may extend the range of applicability of correlation diagrams to processes possessing low point group symmetry. Moreover, it can supplement OCAMS when symmetry arguments alone are inadequate for specifying the optimal reaction path. This latter aspect will be illustrated by singling out energetically preferred geometries for the approach of two H_2 molecules on the potential energy surface for the H_2+D_2 exchange reaction.

2. Correlation Diagrams Using Many Electron Functions

We consider a reactant of nuclear configuration R which is to be converted into a product of nuclear geometry P. Along the pathway we maintain a point group G common to reactants and products. This implies that we impose a nuclear displacement along a symmetry coordinate S which is totally symmetric in the adopted group G. We assume that the Schrödinger equations for the reactant and product nuclear configurations have been solved

$$H_R|R\rangle = E_R|R\rangle \tag{1}$$

$$H_P|P\rangle = E_P|P\rangle \tag{2}$$

In the Hamilton operators H_R and H_P, the nuclear coordinates have fixed values for the geometries R and P, respectively. Thus, these nuclear arrangements are considered to be static, so the kinetic energy operator for the nuclear motion is absent in H_R and H_P. Our primary aim is to devise a criterion for determining whether the retention of G is energetically favourable. For this purpose we consider an intermediate nuclear geometry I, located between reactants and products on the potential energy surface and also having the symmetry of G (see Fig. 1). As the wavefunction we employ the following variational ansatz [5]

$$|I\rangle = C_R(I)|R\rangle + C_P(I)|P\rangle \tag{3}$$

The wavefunction $|I\rangle$ for the nuclear arrangement I is a superposition of wavefunctions calculated for the different geometries R and P, but the coefficients $C_R(I)$ and $C_P(I)$ vary with the geometry I selected. Consequently, $|I\rangle$ has the flexibility to become $|R\rangle$ and $|P\rangle$ when I coincides with the reactant or product

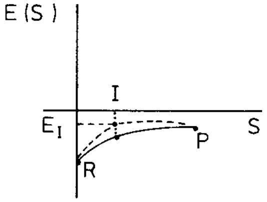

Fig. 1. Change of the nuclear geometry from reactants R to products P along a totally symmetric coordinate S in the retained group G. The continuous line is the exact potential energy surface; the dotted line represents the surface when the variational ansatz (3) is used

geometry, respectively. Minimization of the energy leads to the eigenvalue problem

$$\left(\begin{array}{c|c}\langle R|H(I)|R\rangle & \langle R|H(I)|P\rangle \\ \langle P|H(I)|R\rangle & \langle P|H(I)|P\rangle\end{array}\right)\left(\begin{array}{c}C_R(I) \\ \hline C_P(I)\end{array}\right)=\left(\begin{array}{c|c}1 & \langle R|P\rangle \\ \langle P|R\rangle & 1\end{array}\right)\left(\begin{array}{c}C_R(I) \\ \hline C_P(I)\end{array}\right)E(I) \tag{4}$$

The dependence of the operator and the coefficients on the geometry I is indicated by (I). For different I, Eq. (4) can be solved for the corresponding $E(I)$ values. It follows from the variational ansatz (3) that the energy $E(I)$ is always higher than the exact energy, as indicated in Fig. 1. We assume that the exact potential energy surface (continuous line in Fig. 1) can be adequately represented by the curve passing through all of the intermediate $E(I)$ values (dotted line in Fig. 1). It is clear from the form of Eq. (3) that this assumption is valid when the geometry I is close to that of either the reactant or the product.

An analytic expression for $E(I)$ is derived by means of a simple partitioning [6] as indicated in Eq. (4).

$$E(I)=\underset{\text{(a)}}{\langle R|H(I)|R\rangle}+\underset{\text{(b)}}{\frac{(\langle R|H(I)|P\rangle-\langle R|P\rangle E(I))^2}{E(I)-\langle P|H(I)|P\rangle}} \tag{5}$$

This simple perturbational expression for $E(I)$ is implicit, but it is exact for the eigenvalue problem (4). An advantage of Eq. (5) is the partitioning of $E(I)$ into two contributions, (a) and (b), each of which has a characteristic meaning. By use of the results derived in the appendix, we find that the expectation values $\langle R|H(I)|R\rangle$ and $\langle P|H(I)|P\rangle$ are upper bounds to the energy $E(I)$. Consequently, (a) is always higher than $E(I)$, whereas (b) is negative, due to its negative denominator and positive numerator. Thus, it is the latter term which facilitates a distortion along the totally symmetric pathway because it is always energy-decreasing. This conclusion is closely related to the results derived by D. M. Silver [5], who solved Eq. (4) by means of the quadratic equation, and derived the energy-lowering contribution at a point I at which $\langle R|H(I)|R\rangle$ has the same value as $\langle P|H(I)|P\rangle$. The conceptual advantage of the perturbational expression (5) is the occurrence of the energy lowering contribution (b), which is valid for all intermediate nuclear arrangements I. The physical meaning of (a) and (b) is similar to the meaning of the perturbational expression for the force constant in the Bader–Pearson Concept [7]. Contribution (a) contains the wavefunctions of the reactants but the operator $H(I)$ for the geometry I. Consequently, (a) reflects the effect on the energy of displacing the nuclei towards I, but without readjusting the wavefunction to the new geometry. Thus, (a) resembles the energy contribution arising from the "classical force constant term" which describes a nuclear motion in the unrelaxed electronic charge distribution [8]. The energy term (b) is stabilizing in a way similar to the energy referring to the relaxational contribution to the force constant [8] employed in the Bader–Pearson concept. However, the latter procedure is based on a harmonic potential model, with small nuclear distortions, whereas Eq. (5) is valid for arbitrarily large displacements from R towards P.

On the basis of the above analysis, we conclude that a nuclear distortion from R to P is energetically favourable provided the energy-decreasing contribution (b) does not vanish. The analytic form of (b) leads immediately to a group theoretical selection rule which has been derived in a somewhat different way by Silver [5]: Since the operator $H(I)$ is always totally symmetric in the group adopted, we conclude: *The retention of a group G from R to P can be energetically favourable, provided that the product of the wavefunctions $|R\rangle$ and $|P\rangle$ transforms totally symmetrically.* This is the case when the direct product $\Gamma_R \times \Gamma_P$ of the irreducible representations to which $|R\rangle$ and $|P\rangle$ belong, respectively, contains the totally symmetric representation. If a group G is retained where $|R\rangle$ and $|P\rangle$ transform differently, (b) vanishes by symmetry. The retention of such a group G is therefore energetically unfavourable. For excited state and radical potential energy surfaces, $|R\rangle$ and $|P\rangle$ might transform differently and the rule can be discriminative. For closed shell ground-state surfaces, however, $|R\rangle$ and $|P\rangle$ are always totally symmetric in any group retained. Therefore, the selection rule is indiscriminative for closed shell ground-state potential energy surfaces. This latter situation is taken up in the next section.

3. Correlation Diagrams Using Molecular Orbitals

The formula for the energy $E(I)$ of a nuclear arrangement I can be reformulated using a partitioning of the operator $H(I)$

$$H(I) = H_R + V(I) \tag{6}$$

Thus, $H(I)$ is decomposed into the operator H_R for the reactant geometry R and the one-electron operator $V(I)$ representing the change in the nuclear-electron attraction when the nuclei are displaced from R to I. Using Eqs (6) and (1), we reformulate Eq. (5) as

$$E(I) = \underbrace{[E_R + \langle R|V(I)|R\rangle]}_{\text{(a)}} + \underbrace{\frac{[\langle R|V(I)|P\rangle - \langle R|P\rangle(E(I) - E_R)]^2}{E(I) - \langle P|H_R|P\rangle - \langle P|V(I)|P\rangle}}_{\text{(b)}}. \tag{7}$$

Our major aim is to derive symmetry conditions which force (b), the reformulated relaxational term of Eq. (5), to vanish.

The eigenfunctions $|R\rangle$ and $|P\rangle$ are considered as expanded into the complete set of Slater determinants $|\tilde{R}_j\rangle$ and $|\tilde{P}_j\rangle$, respectively.

$$|R\rangle = a_0|\tilde{R}\rangle + \sum_{j=1}^{\infty} a_j|\tilde{R}_j\rangle \approx |\tilde{R}\rangle \tag{8a}$$

$$|P\rangle = b_0|\tilde{P}\rangle + \sum_{j=1}^{\infty} b_j|\tilde{P}_j\rangle \approx |P\rangle \tag{8b}$$

For closed shell ground-state potential energy surfaces, we approximate $|R\rangle$ and $|P\rangle$ by the predominating closed shell Hartree–Fock wavefunctions $|\tilde{R}\rangle$ and $|\tilde{P}\rangle$, respectively (see Eq. (8)). Now, we consider the corresponding expectation value $\langle\tilde{R}|V(I)|\tilde{P}\rangle$ and the overlap integral $\langle\tilde{R}|\tilde{P}\rangle$ occurring in the numerator of (b) in Eq. (7). These integrals have to be evaluated using nonorthogonal closed shell determinantal wavefunctions, because $|\tilde{R}\rangle$ and $|\tilde{P}\rangle$ are calculated for the different reactant and product nuclear geometries. Since $V(I)$ is a one-electron operator, we can apply the standard procedure [9]

$$\langle\tilde{R}|V(I)|\tilde{P}\rangle = \sum_{i}^{m}\sum_{j}^{m} \langle r_i|V(I)|p_j\rangle(-1)^{i+j}\,(\mathrm{Det}\,\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij})^2 \tag{9}$$

where m designates the number of doubly occupied Hartree–Fock orbitals $|r_i\rangle$ and $|p_j\rangle$ of reactant and product, respectively. All m occupied orbitals of reactant and product are arranged in the row vectors $|\boldsymbol{r}\rangle$ and $|\boldsymbol{p}\rangle$, respectively. Consequently $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ is an $m \times m$ overlap matrix and $\mathrm{Det}\,\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij}$ represents the determinant of $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ where row i and column j have been deleted. The overlap integral occurring in (b) of Eq. (7) can be calculated [9] by means of

$$\langle\tilde{R}|\tilde{P}\rangle = (\mathrm{Det}\,\langle \boldsymbol{r}|\boldsymbol{r}\rangle\,\mathrm{Det}\,\langle \boldsymbol{p}|\boldsymbol{p}\rangle)^{1/2}(\mathrm{Det}\,\langle \boldsymbol{r}|\boldsymbol{p}\rangle)^2 = (\mathrm{Det}\,\langle \boldsymbol{r}|\boldsymbol{p}\rangle)^2 \tag{10}$$

where the property has been used that $\langle \boldsymbol{r}|\boldsymbol{r}\rangle$ and $\langle \boldsymbol{p}|\boldsymbol{p}\rangle$ are unit matrices. Now, we consider m occupied orbitals of reactant and product, each of which is calculated at its own geometry. However, we classify them in the common group G, which is retained along the adopted pathway. In Fig. 2, we have ordered them according to their irreducible representations Γ_i, rather than according to their energies. Moreover, Fig. 2 is based on the symmetry conditions for a symmetry-forbidden pathway where an occupied (unoccupied) orbital of the reactant with symmetry Γ_u (Γ_t) is transformed into an unoccupied (occupied) orbital of the product. The number of orbitals of species Γ_i on the reactant side of the diagram equals the number on the product side for all Γ_i except Γ_t and Γ_u. For Γ_t we have one orbital less for the reactant than for the product (see Fig. 2); the reverse situation holds for the irreducible representation Γ_u (see Fig. 2).

In the following, we relate the magnitude of $\langle\tilde{R}|V(I)|\tilde{P}\rangle$ and $\langle\tilde{R}|\tilde{P}\rangle$ appearing in (b) of Eq. (7) to the symmetry conditions represented in Fig. 2. Due to symmetry, the $m \times m$ overlap matrix $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ possesses the block form shown in Fig. 3.

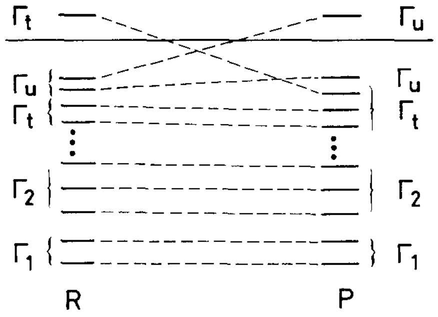

Fig. 2. Symmetry of reactant R and product P orbitals for a symmetry forbidden ground state pathway. The molecular orbitals are ordered according to irreducible representations Γ_i of G and not according to their energies. The long continuous line separates the occupied and unoccupied orbitals

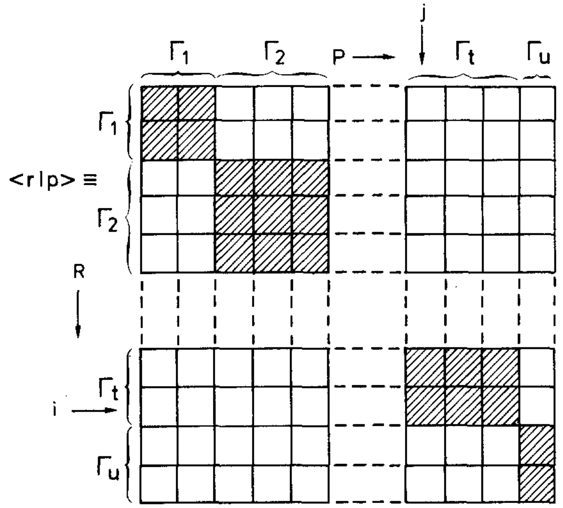

Fig. 3. Form of the overlap matrix $\langle r|p\rangle$ for a symmetry forbidden ground state pathway

For the evaluation of Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij}$ occurring in Eq. (9) we can use the Laplacian expansion of determinants in its generalized form [10]

$$\operatorname{Det}\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij} = \sum_{\rho} (-1)^{(\Sigma r+\Sigma c)} \operatorname{Det}^{c_1,\ldots,c_{nr}}_{r_1,\ldots,r_{nr}} \langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij} \operatorname{Det}^{c_{\text{rem}}}_{r_{\text{rem}}} \langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij} . \tag{11}$$

Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij}$ is expanded into the minors of nr rows indicated by the symbol $r_1, \ldots, r_{nr}$; the upper index $c_1, \ldots, c_{nr}$ designates a particular combination ρ of nr columns. The sum over ρ in (11) is over all possible sets of the indices $c_1 \ldots c_{nr}$. The indices r_{rem} and c_{rem} designate a determinant containing all remaining rows and columns, respectively. Expanding Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij}$ in the minors of the last two rows (see Fig. 3), we recognize that

$$\operatorname{Det}^{c_1,\ldots,c_{nr}}_{r_1,\ldots,r_{nr}} \langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij} = 0 \tag{12}$$

holds, because for every ρ the 2×2-determinant, which appears as factor in Eq. (11), contains either a zero column or a zero row; consequently, all Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{ij}$ vanish. Thus, all matrix elements $\langle r_i|V(I)|p_j\rangle$ occurring in (9) are multiplied by zero, and the expectation value $\langle \tilde{R}|V(I)|\tilde{P}\rangle$ appearing in Eq. (7b) vanishes. For the evaluation of the overlap integral $\langle \tilde{R}|\tilde{P}\rangle$ we have to determine Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ (see Eq. (10)). Using the block form depicted in Fig. (3) and expanding Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ into the minors of the last two rows by means of Eq. (11), we see that $\langle \tilde{R}|\tilde{P}\rangle$ is zero due to symmetry. Consequently, the energy lowering contribution (b) of Eq. (7), which makes the potential energy surface energetically favourable, vanishes.

We are now in a position to formulate a symmetry rule for nuclear motions along a ground state potential energy surface: *The retention of a point group G is energetically unfavourable whenever G induces an overlap matrix $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ between the occupied orbitals of reactants and products with two rectangular blocks.* Such a block form is based on a molecular orbital correlation diagram in which at least one pair of orbitals is not in correlation. Retention of a group G which causes a block-diagonal overlap matrix containing only quadratic blocks can be energetically favourable, because it is only in this case that symmetry does not force (b) of Eq. (7) to vanish. Such a block-diagonal form corresponds to a correlation diagram were all occupied orbitals are in correlation.

As pointed out in Sect. 2, the many electron closed shell wavefunctions $|R\rangle$ and $|P\rangle$ transform totally symmetric in any group G. Consequently, a pathway along which any G is retained is allowed by state symmetry. However, we have now shown that a discriminative selection rule exists at the molecular orbital level. Thus, a path which retains a particular group G may be symmetry-allowed with respect to the many-electron functions $|R\rangle$ and $|P\rangle$, but symmetry-forbidden at the molecular orbital level. This finding is a consequence of the hierarchy of symmetry rules, which was discussed in detail by D. M. Silver [5].

4. Symmetry Lowering and Energetically Favoured Nuclear Distortions

Consider a reaction path from reactants to products, which has been characterized as symmetry-forbidden in the group G retained. As outlined in Sect. 2, $|R\rangle$ and $|P\rangle$ for reactant and product, respectively, transform according to different irreducible representations of G. Consequently, the energy-decreasing contribution (b) of Eq. (5) vanishes. However, a pathway resulting from a reduction of symmetry from that of the group G into one of its subgroup G_k might be energetically favourable. In the following analysis we attempt to single out which subgroup G_k of G must be maintained along the preferred new pathway.

For this purpose we rewrite Eq. (5)

$$E(I)=\langle R|H(I)|R\rangle+\frac{\langle R|H(I)-E(I)|P\rangle^2}{E(I)}\left(1-\frac{\langle P|H(I)|P\rangle}{E(I)}\right)^{-1}. \qquad (13)$$

Assuming that $\langle P|H(I)|P\rangle$, like $E(I)$, is a negative quantity and using the fact that $\langle P|H(I)|P\rangle$ is an upper bound to $E(I)$ (see appendix) we have

$$\frac{\langle P|H(I)|P\rangle}{E(I)}\leqq 1. \qquad (14)$$

If this quantity is less than 1, we can expand Eq. (13) in a power series

$$E(I) = \langle R|H(I)|R\rangle + \frac{1}{E(I)}\langle R|H(I) - E(I)|P\rangle^2 \times\left(1 + \frac{\langle P|H(I)|P\rangle}{E(I)} + \frac{\langle P|H(I)|P\rangle^2}{E(I)^2} + \cdots\right). \qquad (15)$$

Let us now consider a nuclear arrangement I which is close to the nuclear geometry of the reactant (see Fig. 1). In this case $E(I)$ should not be very different from E_R, so we can replace $E(I)$ in Eq. (15) by E_R to obtain an approximate explicit expression for $E(I)$

$$\tilde{E}(I) = \langle R|H(I)|R\rangle + \frac{1}{E_R}\langle R|H(I) - E_R|P\rangle^2 + \frac{1}{E_R^2}\langle R|H(I) - E_R|P\rangle^2\langle P|H(I)|P\rangle \qquad (16)$$

where we have truncated the power series in Eq. (15) after the second term. If we use the decomposition (6) of $H(I)$ we derive

$$\begin{aligned}\tilde{E}(I) = E_R + &\underset{(a)}{\langle R|V(I)|R\rangle}\\ &+ \frac{1}{E_R}\underset{(b)}{\langle R|V(I)|P\rangle^2}\\ &+ \frac{1}{E_R^2}\underset{(c)}{\langle R|V(I)|P\rangle^2\langle P|H_R|P\rangle} \qquad (17)\\ &+ \frac{1}{E_R^2}\underset{(d)}{\langle R|V(I)|P\rangle^2\langle P|V(I)|P\rangle}\end{aligned}$$

where (b–d) in Eq. (17) approximate the energy lowering contribution (b) of Eq. (7).

In the group retained, $|R\rangle$ and $|P\rangle$ transform differently along the assumed symmetry-forbidden pathway, so the stabilizing terms (b–d) vanish by symmetry. However, the nuclei may deviate along a non-totally symmetric coordinate S_j, inducing a subgroup G_k in which (b–d) do not vanish. For the determination of such an S_j, we consider the operator $V(I)$ after a displacement along S_j by an amount ΔS_j and expand $V(I + \Delta S_j)$ into a Taylor series at I.

$$V(I + \Delta S_j) = V(I) + \left(\frac{\partial V}{\partial S_j}\right)_I \Delta S_j + \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial S_j^2}\right)_I \Delta S_j^2 + \cdots \qquad (18)$$

Substituting Eq. (18) into Eq. (17) we obtain the total energy $E(I+\Delta S_j)$ at the displaced nuclear geometry $(I+\Delta S_j)$ up to terms proportional to ΔS_j^2

$$\begin{aligned} E(I+\Delta S_j) = {} & \underset{(a)}{E(I)} + \underset{(b)}{\langle R|\left(\frac{\partial V}{\partial S_j}\right)_I|R\rangle \Delta S_j} \\ & + \underset{(c)}{\frac{1}{E_R^2}\langle R|V(I)|P\rangle^2 \langle P|\left(\frac{\partial V}{\partial S_j}\right)_I|P\rangle \Delta S_j} \\ & + \underset{(d)}{\frac{1}{2E_R^2}\langle R|V(I)|P\rangle^2 \langle P|\left(\frac{\partial^2 V}{\partial S_j^2}\right)_I|P\rangle \Delta S_j^2} + \underset{(e)}{\tfrac{1}{2}\langle R|\left(\frac{\partial^2 V}{\partial S_j^2}\right)_I|R\rangle \Delta S_j^2} \\ & + \underset{(f)}{\frac{1}{E_R}\langle R|\left(\frac{\partial V}{\partial S_j}\right)_I|P\rangle^2 \Delta S_j^2} + \underset{(g)}{\frac{1}{E_R^2}\langle R|\left(\frac{\partial V}{\partial S_j}\right)_I|P\rangle^2 \langle P|H(I)|P\rangle \Delta S_j^2}. \end{aligned} \tag{19}$$

The first contribution (a) is the energy of the nuclear arrangement with geometry I, which is located on the unfavourable high symmetry pathway where $|R\rangle$ and $|P\rangle$ belong to different irreducible representations of G. Moreover, we presuppose that $|R\rangle$ transforms not as a multi-dimensional representation. Thus, a symmetry lowering arising from the static Jahn–Teller effect [11] is excluded from the following considerations. Based on this assumption, the second term (b) vanishes, since the operator $(\partial V/\partial S_j)_I$ transforms as S_j, which is non-totally symmetric in the unfavourable group G. The contributions (c) and (d) are zero since the integrals $\langle R|V(I)|P\rangle$ vanish. Symmetry alone does not force (e) to become zero, because $(\partial^2 V/\partial S_j^2)_I$ is always totally symmetric for any S_j. The discriminative contributions are (f) and (g) which lower the energy when we displace from I to $(I+\Delta S_j)$. We see immediately that (f) and (g) vanish, unless the triple direct product $\Gamma_R \times \Gamma_{S_j} \times \Gamma_P$ contains the totally symmetric representation. Thus, we derive a symmetry-lowering selection rule when many-electron wavefunctions $|R\rangle$ and $|P\rangle$ are employed: *A pathway which is totally symmetric in the group G and is symmetry-forbidden can be avoided by lowering the symmetry along a symmetry coordinate S_j for which the triple direct product of the representations of the reactant, the coordinate and the product contains the totally symmetric representation of G*:

$$\Gamma_R \times \Gamma_{S_j} \times \Gamma_P \supset \Gamma_1. \tag{20}$$

Moreover, if $|R\rangle$ and $|P\rangle$ belong to one-dimensional irreducible representations, the symmetry of the many-electron overlap density function $\psi_R^* \psi_P$ contained in the integral $\langle R|(\partial V/\partial S_j)_I|P\rangle$ determines the symmetry of the preferred non-totally symmetric coordinate

$$\Gamma_{S_j} = \Gamma_R \times \Gamma_P. \tag{21}$$

Eqs. (20) and (21) are the operational rules of the symmetry lowering OCAMS procedure, as applied to many-electron functions [4]. Once more, as in Sect. 2, the rule is not discriminative when both R and P are closed shell ground states, which are necessarily totally symmetric.

5. Symmetry Lowering on Ground State Potential Energy Surfaces

In Sect. 3 we have illustrated that the retention of a group G for nuclear motions on the ground state potential energy surface is energetically unfavourable whenever the overlap matrix $\langle \mathbf{r}|\mathbf{p}\rangle$ between occupied molecular orbitals of reactants and products contains two rectangular blocks (see Fig. 3). Here, we show how to choose the non-totally symmetry coordinate S_j along which the nuclei can deviate in order to avoid the unfavourable pathway. For this purpose we consider the integral $\langle R|(\partial V/\partial S_j)_I|P\rangle$, which appears in the energy-lowering terms (f) and (g) of Eqn. (19). Again, we approximate $|R\rangle$ and $|P\rangle$ by the closed shell Hartree–Fock wavefunctions $|\tilde{R}\rangle$ and $|\tilde{P}\rangle$ for reactants and products, respectively. Using this simplification, we can apply the standard procedure [9] to evaluate the integral

$$\langle \tilde{R}| \left(\frac{\partial V}{\partial S_j}\right)_I |\tilde{P}\rangle = \sum_k^m \sum_l^m \langle r_k| \left(\frac{\partial V}{\partial S_j}\right)_I |p_l\rangle (-1)^{k+l} \, (\mathrm{Det}\,\langle \mathbf{r}|\mathbf{p}\rangle_{kl})^2 \tag{22}$$

The indices k and l run over all m doubly occupied orbitals. Consider a symmetry coordinate S_j in the group G, whose symmetry is such that

$$\Gamma_t \times \Gamma_{S_j} \times \Gamma_u \supset \Gamma_1 \tag{23}$$

holds.

Thus, the symmetry of S_j is determined by the symmetries Γ_t and Γ_u of the pair of non-correlating orbitals which produce the two rectangular blocks in Fig. 3. Using such an S_j, the matrix $\langle \mathbf{r}|(\partial V/\partial S_j)_I|\mathbf{p}\rangle$ has the form given in Fig. 4, in which

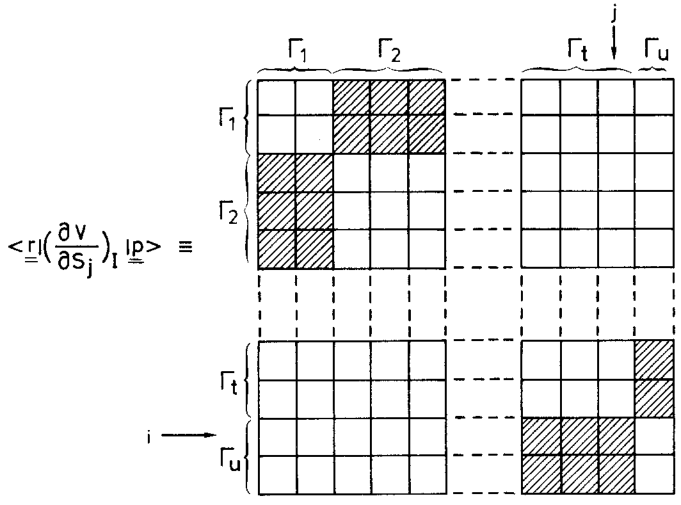

Fig. 4. Form of the matrix $\langle \mathbf{r}|(\partial V/\partial S_j)_I|\mathbf{p}\rangle$ for a energetically favourable deviation from G along a non-totally symmetric symmetry coordinate S_j

the matrix elements $\langle r_k|(\partial V/\partial S_j)_I|p_l\rangle$ vanish unless the triple direct product $\Gamma_k \times \Gamma_{S_j} \times \Gamma_l$ contains the totally symmetric representation. Using the block form depicted in Fig. 4 for the evaluation of $\langle \tilde{R}|(\partial V/\partial S_j)_I|\tilde{P}\rangle$ by means of (22), we see that each of the non-vanishing matrix elements $\langle r_k|(\partial V/\partial S_j)_I|p_l\rangle$ located in the lowest rectangular block is multiplied by a non-vanishing determinant Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{kl}$. Any other non-vanishing matrix element, such as those in the upper corner of Fig. 4, is multipled by a vanishing determinant Det $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{kl}$. This is due to the fact that it is only in the former case that $\langle \boldsymbol{r}|\boldsymbol{p}\rangle_{kl}$ is block-diagonal, with only quadratic blocks. Consequently, the energy lowering terms (f) and (g) of Eq. (19) are non-zero by symmetry, and a nuclear displacement along S_j is energetically favourable by virtue of the induced interaction between the non-correlating orbitals. These results lead to a systematic procedure for making a symmetry-forbidden pathway symmetry-allowed: *If a nuclear displacement on the ground-state potential energy surface is symmetry-forbidden when a group G is preserved, the nuclei may deviate along a non-totally symmetric coordinate S_j, which lowers the symmetry of the pathway to that of the subgroup G_k of G which is the kernel of* Γ_{S_j} [4].

The symmetry Γ_{S_j} of the favourable nuclear displacement is such that the triple direct product $\Gamma_t \times \Gamma_{S_j} \times \Gamma_u$ contains the totally symmetric representation as indicated in Eq. (23).

Thus, from the symmetries of orbitals which are not in correlation, we can determine a nuclear pathway which is symmetry-allowed and energetically more favourable. Eq. (23) is the symmetry lowering OCAMS rule [3] on the molecular orbital level, which we have deduced from the requirement that the nuclear motions on the ground state potential energy surface should be energetically favourable.

6. Correlation Diagrams without using Symmetry

In the previous sections we have illustrated how the requirement of energetically favourable nuclear motions on a potential energy surface is related to the symmetry maintained along the pathway. Specifically, we have deduced the OCAMS rules for choosing those nuclear motions which can convert a symmetry-forbidden path into one that is symmetry allowed. An essential premise of this procedure is that both the reactant and the product have a sufficient number of symmetry elements to make the application of group theory efficient. However, many molecules of chemical interest are insufficiently symmetrical for the rules derived above to be adequately discriminative. Therefore, a procedure which is not based on group theoretical symmetry arguments is desirable for selecting favourable nuclear motions.

We consider a correlation diagram between the occupied orbitals of reactants and products where a particular mode of nuclear motion has been arbitrarily selected. Pointwise calculations may indicate that a pair of occupied orbitals of reactant and product are not in correlation. In the following, we relate this information about non-correlation to the magnitude of the energy-decreasing contribution (b) in Eq. (7) by making the following assumptions:

(1) The overlap integral $\langle r_i|p_j\rangle$ is larger for a pair ij of correlating molecular orbitals than for a pair which does not correlate.

This supposition is based on the idea that the location of nodal surfaces of correlating molecular orbitals remains almost unchanged in space. Conversely, non-correlating orbitals are assumed to have nodal surfaces in different spatial regions. These premises imply that the overlap integral between correlating orbitals is large whereas that between a pair of non-correlating orbitals is small.

(2) The integral $\langle r_i|V(I)|p_j\rangle$ is larger for a pair ij of orbitals which correlate than for a pair of non-correlating orbitals.

Since the nodal surfaces of the correlating orbitals $|r_i\rangle$ and $|p_j\rangle$ are assumed to be retained, the function $r_i^*(1)p_j(1)$ possesses the same sign in all spatial regions. Consequently, the nuclear positions appearing in $V(I)$ are in spatial regions where $r_i^*(1)p_j(1)$ has the same sign. Therefore, the integral $\langle r_i|V(I)|p_j\rangle$ should be large. In contrast, when i and j refer to a pair of non-correlating orbitals, the nuclei may be located in spatial regions where the function $r_i^*(1)p_j(1)$ has a different sign and the integral $\langle r_i|V(I)|p_j\rangle$ can be assumed to be negligible.

Consider a correlation diagram where the mth pair of orbitals is not in correlation. By assumptions (1) and (2), the matrices $\langle \mathbf{r}|V(I)|\mathbf{p}\rangle$ and $\langle \mathbf{r}|\mathbf{p}\rangle$ have approximate diagonal form, where the elements $\langle r_m|V(I)|p_m\rangle$ and $\langle r_m|p_m\rangle$ are small, as indicated in Fig. 5. The application of Eqs. (9) and (10) for the evaluation of the integrals $\langle \tilde{R}|V(I)|\tilde{P}\rangle$ and $\langle \tilde{R}|\tilde{P}\rangle$, respectively, occurring in (b) of Eq. (7) shows that the contribution (b) is small. This is due to the fact that for $i = 1, 2, \ldots, m-1$ all Det $\langle \mathbf{r}|\mathbf{p}\rangle_{ii}$ contain a row with almost zero matrix elements (see Fig. 5); for $i = m$, Det $\langle r|p\rangle_{mm}$ is multiplied by $\langle r_m|V(I)|p_m\rangle$ which is small (see Fig. 5). Consequently, the adopted nuclear pathway is energetically unfavourable, since one pair of occupied orbitals of reactants and products has a small overlap. This conclusion, which is central to the mapping analysis proposed by Trindle [12], may be stated: *A reaction path is unfavourable when two orbitals do not map onto each other, as indicated by a small overlap integral* $\langle r_m|p_m\rangle$. Here, we have related this postulate to the magnitude of the energy-decreasing contribution (b) of Eq. (7), which is small when $|r_m\rangle$ and $|p_m\rangle$ do not map onto one another.

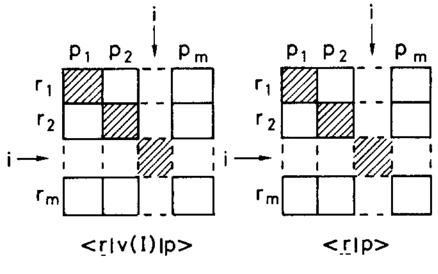

Fig. 5. Schematic form of the matrices $\langle \mathbf{r}|V(I)|\mathbf{p}\rangle$ and $\langle \mathbf{r}|\mathbf{p}\rangle$ when the orbitals r_m and p_m are not in correlation

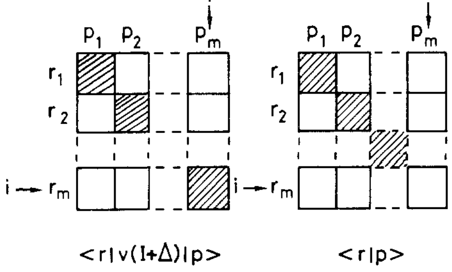

Fig. 6. Schematic form of the matrices $\langle r|V(I+\Delta)|p\rangle$ and $\langle r|p\rangle$ after a nuclear distortion suggested by the form of the overlap density function $r_m^*(1)p_m(1)$

Now, we attempt to find the nuclear displacement Δ which avoids the unfavourable pathway. We propose the following general procedure: *Deviate from the unfavoured path as indicated by the form of the overlap density function $r_m^*(1)p_m(1)$ of the non-correlating occupied orbitals $|r_m\rangle$ and $|p_m\rangle$. In particular, move the nuclei into those spatial regions where $r_m^*(1)p_m(1)$ has a high functional value and the same sign.* At such a displaced geometry $(I+\Delta)$, the integral $\langle r_m|V(I+\Delta)|p_m\rangle$ should be large, because the nuclear arrangement $(I+\Delta)$ is adapted to the form of $r_m^*(1)p_m(1)$. Comparison of Fig. 6 with Fig. 5 shows that a new non-vanishing element appears in the matrix $\langle r|V(I+\Delta)|p\rangle$ but the overlap matrix $\langle r|p\rangle$ remains unaffected because the orbitals are independent of the geometry $I+\Delta$ selected. Application of Eq. (9) to determine $\langle\tilde{R}|V(I+\Delta)|\tilde{P}\rangle$ illustrates that the energy-decreasing contribution (b) of Eq. (7) is significant because $\langle r_m|V(I+\Delta)|p_m\rangle$ is not small. Therefore, we conclude that a nuclear displacement from I to $I+\Delta$, as indicated by the form of the overlap density function $r_m^*(1)p_m(1)$, is energetically favourable.

7. Favourable Nuclear Motions on the Potential Energy Surface for the Approach of two Hydrogen Molecules

An effective way to single out favourable nuclear motions on a potential energy surface are the symmetry based OCAMS rules [3, 13, 14], which we have derived above by the requirement of energetically favourable nuclear motions on the potential energy surface. Here, we employ this procedure to determine the most favourable geometry of approach of two hydrogen molecules in their electronic ground state. If the information derived from symmetry considerations alone is insufficient, we determine the favourable nuclear motions by referring to the form of the overlap density function between non-correlating orbitals, as proposed in Sect. 6. The qualitative results are compared with the H_2+H_2 potential energy surface which has been calculated with high accuracy [15, 16, 17].

The obvious initial pathway to adopt is the rectangular approach of two hydrogen molecules, retaining D_{2h} symmetry. The correlation diagram for the energies of the molecular orbitals has been calculated *ab initio* using the STO-3G basis set [18] (see Fig. 7). For the calculations, the intramolecular H-H distances were fixed at 0.712 Å, which is the STO-3G equilibrium value [19]. The intermolecular distance $R(H_2-H_2)$ has been varied from 2.0 Å to 0.5 Å and the calculated

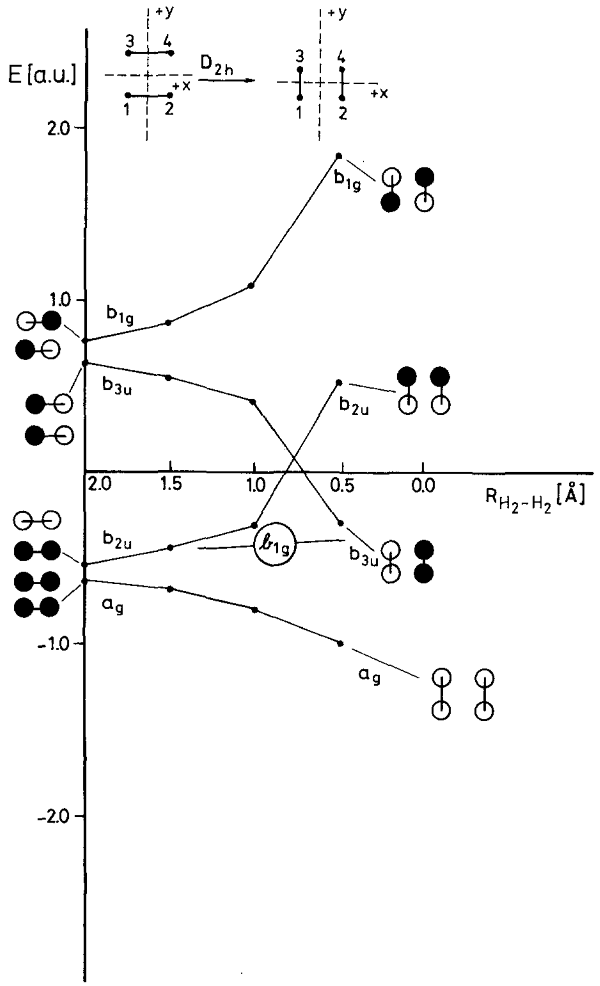

Fig. 7. Correlation diagram of molecular orbitals for a planar D_{2h} approach of two H_2 molecules

points are indicated. Fig. 7 designates the rectangular D_{2h} approach as symmetry-forbidden, because the highest occupied orbitals are not in correlation [20]. This known result [20] is fully supported by the calculations of the ground state potential energy surface for two impinging hydrogen molecules, as performed by D. M. Silver et al. [17]. Over a wide range of intermolecular distances the rectangular approach is the most unfavourable [17].

We are now in a position to exploit the information about non-correlation to determine a pathway for the mutual approach which is symmetry-allowed. For this purpose we apply the symmetry-lowering OCAMS rule, derived in Sect. 5. As the reactant nuclear configuration R we consider the geometry which refers to the left side of the correlation diagram (see Fig. 7). The product nuclear geometry P is the arrangement used for the calculation of the right side of the

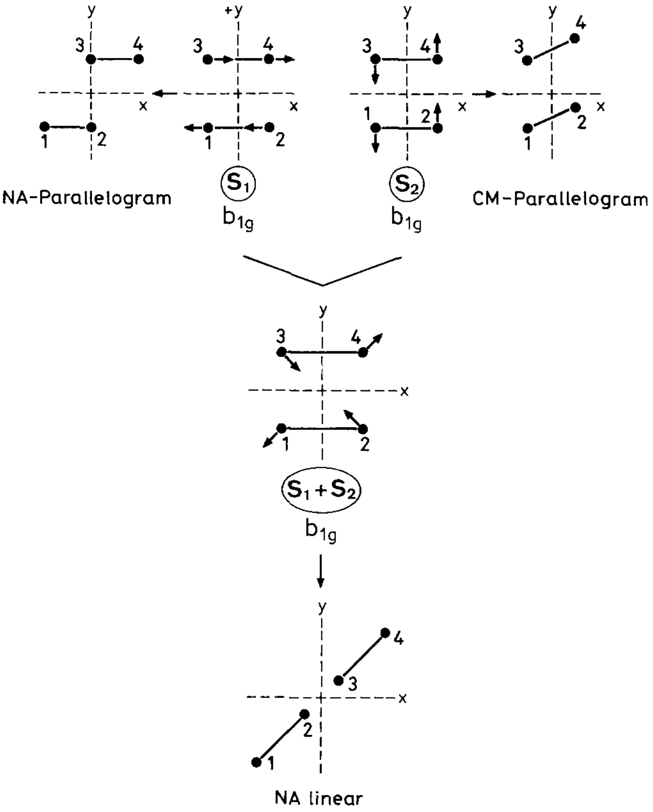

Fig. 8. B_{1g} symmetry coordinates and the resulting nearest atom (NA) and centre of mass (CM) pathways

correlation diagram (see Fig. 7). According to the OCAMS rules, we have to deviate from the D_{2h} pathway along a b_{1g} symmetry coordinate because for this coordinate the triple direct product between the symmetries of the non-correlating orbitals and the symmetry of the distortion yields the totally symmetric representation [3]. In Fig. 8 we have depicted two orthogonal symmetry coordinates S_1 and S_2, both transforming as b_{1g}, and thus reducing the symmetry from D_{2h} to C_{2h}^{z}. Therefore, the favourable nuclear distortion should be a linear combination of the two symmetry coordinates S_1 and S_2, superimposed upon other symmetry coordinates which are totally symmetric in D_{2h}.

A displacement along the "pure" S_1 coordinate would lead to a nearest atom (*NA*) parallelogram orientation, whereas a distortion along S_2 results in a centre of mass (CM) parallelogram orientation. A combination of S_1 and S_2 suggests a nearest atom linear pathway. Thus, we have to determine to what extent S_1 and S_2 are incorporated in the energetically preferred deviation from the D_{2h} pathway. The OCAMS analysis alone is unable to distinguish between the three

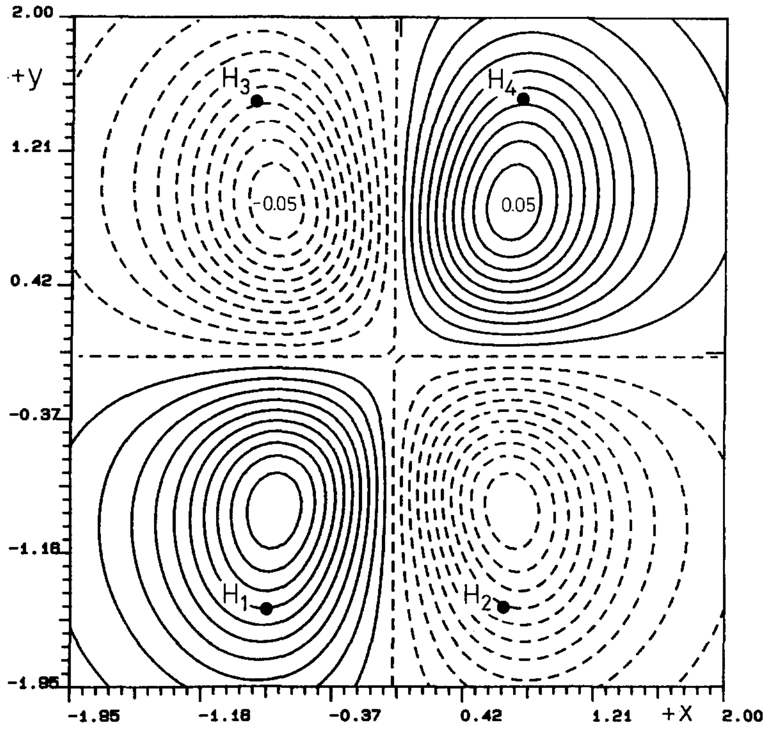

Fig. 9. Overlap density function $r_2(1)p_2(1)$ for the orbitals r_2 and p_2 which are not in correlation when a rectangular D_{2h} pathway is retained. The spacing of lines is 0.005

different pathways, because it only predicts the symmetry species of the displacement. Because of this limitation we supplement OCAMS with the overlap density function approach of Sect. 6.

In Fig. 9 we have depicted contour lines for the overlap density function $r_2(1)p_2(2)$ between the orbitals which are not in correlation, when the D_{2h} pathway is retained. As the reactant nuclear geometry R, we have selected a D_{2h} configuration where the intermolecular distance was fixed at 3.0 a.u. In the product nuclear arrangement P this distance was decreased to 1.0 a.u. In both geometries the intramolecular H–H distance was fixed at 1.345 a.u. which is the STO-3*G* equilibrium value [19]. Moreover, the nuclear positions of the geometry R from which we have to deviate, are also recorded. Inspection of Figs. 8 and 9 indicates that an impinging pathway which brings all four atoms into regions in which the overlap density has the same sign, leads the nuclei along a linear combination of S_1 and S_2, so that they achieve an essentially linear orientation.

Consequently, such a nearest-atom linear pathway should be energetically favourable. These qualitative results are supported by the extensive calculation of D. M. Silver et al. [17]. Over a wide range of intermolecular distances, a pathway with a nearest atom linear orientation of the two hydrogen molecules is indeed the most favourable [17].

8. Conclusion

The results derived above support the expectation that the form of the overlap density function between non-correlating orbitals can be used to supplement OCAMS. Particularly, when OCAMS predicts a symmetry of distortion which may refer to several symmetry coordinates, the form of the overlap density function may be used to select the preferred nuclear pathway. Since the overlap density function procedure is independent of group theoretical symmetry arguments, one may also hope that it is applicable to molecular systems having insufficient symmetry for an orbital symmetry analysis to be useful.

Appendix

In the following discussion we analyse the role of the energy contributions (5a) and (5b) in determining the total energy $E(I)$ of the nuclear arrangement at the geometry I. First, we show that the expectation values $\langle R|H(I)|R\rangle$ and $\langle P|H(I)|P\rangle$ are upper bounds to the energy $E(I)$. Therefore, we consider the total 2×2 secular problem which has been partly treated as Eq. (4) of Sect. 2:

$$\begin{pmatrix} \langle R|H(I)|R\rangle & \langle R|H(I)|P\rangle \\ \langle P|H(I)|R\rangle & \langle P|H(I)|P\rangle \end{pmatrix} \begin{pmatrix} C_{1r} & C_{2r} \\ C_{1p} & C_{2p} \end{pmatrix} = \begin{pmatrix} 1 & \langle R|P\rangle \\ \langle P|R\rangle & 1 \end{pmatrix} \begin{pmatrix} C_{1r} & C_{2r} \\ C_{1p} & C_{2p} \end{pmatrix} \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \tag{1}$$

Moreover, we recall that the lowest eigenvalue E_1 is the energy $E(I)$ at the nuclear geometry I. Now we define a row vector $|\boldsymbol{v}\rangle$ comprising the variational functions $|I_1\rangle$ and $|I_2\rangle$ which are constructed as linear combinations of $|R\rangle$ and $|P\rangle$ as in Eq. (3) of Sect. 2

$$|\boldsymbol{v}\rangle = |I_1\rangle|I_2\rangle = |R\rangle|P\rangle \begin{pmatrix} C_{1r} & C_{2r} \\ C_{1p} & C_{2p} \end{pmatrix} \tag{2}$$

with this $|\boldsymbol{v}\rangle$, the matrix $\langle \boldsymbol{v}|H(I)|\boldsymbol{v}\rangle$ is the diagonal matrix $\boldsymbol{E}_d$ and the overlap matrix $\langle \boldsymbol{v}|\boldsymbol{v}\rangle$ is a unit matrix, thus we have

$$\langle \boldsymbol{v}|H(I)|\boldsymbol{v}\rangle = \boldsymbol{E}_d \tag{3}$$

and

$$\langle \boldsymbol{v}|\boldsymbol{v}\rangle = \mathbf{1} \tag{4}$$

However, we also can perform the inverse transformation

$$|R\rangle|P\rangle = |I_1\rangle|I_2\rangle \begin{pmatrix} t_{11} & t_{21} \\ t_{12} & t_{22} \end{pmatrix}. \tag{5}$$

Moreover, we have

$$\langle R|R\rangle = T_1^{+} \langle \boldsymbol{v}|\boldsymbol{v}\rangle T_1 = t_{11}^2 + t_{12}^2 = 1, \tag{6}$$

where T_1 is the first column of the transformation matrix occurring in Eq. (5).

Now, we can use Eqs. (5) and (3) to determine $\langle R|H(I)|R\rangle$:

$$\langle R|H(I)|R\rangle = \sum_{i=j}^{2} \sum_{j=1}^{2} t_{1i} t_{1j} \langle I_i|H(I)|I_j\rangle = t_{11}^2 E_1 + t_{12}^2 E_2 \tag{7}$$

If we substract E_1 from both sides of Eq. (7) and use Eq. (6), we find that

$$\langle R|H(I)|R\rangle - E_1 = t_{11}^2 E_1 + t_{12}^2 E_2 - (t_{11}^2 + t_{12}^2) E_1 = t_{12}^2 (E_2 - E_1). \tag{9}$$

Now, we assume that the upper eigenvalue E_2 always satisfies $E_2 > E_1$, where E_1 is the lower eigenvalue. This implies that $(E_2 - E_1)$ is always positive.

Recalling that $E_1 \equiv E(I)$, we find that

$$\langle R|H(I)|R\rangle - E(I) \geqq 0, \tag{10}$$

and in a similar way

$$\langle P|H(I)|P\rangle - E(I) \geqq 0. \tag{11}$$

Thus, $\langle R|H(I)|R\rangle$ and $\langle P|H(I)|P\rangle$ are upper bounds to the energy $E(I)$. Note that Eqs. (10) and (11) follow from the theorem that the lowest eigenvalue of a hermitian matrix is always larger than the largest diagonal matrix element [21]. Moreover, Eqs. (10) and (11) are also consequences of the theorem of Hylleras and Undheim [22]. Using the derived results we find the energy contribution (5a) of Sect. 2 as lying above the energy $E(I)$ of the nuclear arrangement I, whereas (5b) is always energy decreasing and makes the nuclear displacement energetically favourable. This is due to the fact that the denominator of (5b) is negative, whereas the numerator is positive.

Acknowledgement. The authors appreciate many stimulating discussions with Prof. O. E. Polansky and Prof. J. Katriel. Valuable comments of Dr. H. Kupka, Dr. F. Mark and Dr. H. Barentzen are also gratefully acknowledged.

One of us (E.A.H.) acknowledges support from The Fund for Promotion of Research at the Technion.

References

1. Woodward, R. B., Hoffmann, R.: "The conservation of orbital symmetry. New York: Academic Press, (1969)
2. Buenker, R. J., Peyerimhoff, S. D.: Chem. Rev. **74**, 127 (1974)
3. Halevi, E. A.: Helv. Chim. Acta **58**, 2136 (1975)
4. Katriel, J., Halevi, E. A.: Theoret. Chim. Acta (Berl.) **40**, 1 (1975)
5. Silver, D. M.: J. Am. Chem. Soc. **96**, 5959 (1974)
6. Löwdin, P. O.: J. Chem. Phys., **19**, 1396 (1951); McWeeny, R., Sutcliffe, B. T.: Methods of molecular quantum mechanics, London: Academic Press, 1969, p. 36.
7. Pearson, R. G.: Symmetry rules for chemical reactions, New York: Wiley, 1976
8. Salem, L.: Chem. Phys. Letters **3**, 99 (1969)
9. Slater, J. C.: Quantum theory of molecules and solids, Vol. 1, App. 9, p. 285. New York: McGraw-Hill, 1963
10. See for example: Ayres, F.: Outline of theory and problems of matrices, New York: p. 33. Schaum Publishing Co., 1962

11. See for example: Ballhausen, C. J.: Introduction to ligand field theory, p. 193–196. New York: McGraw-Hill Co., 1962; Englman, R.: The Jahn Teller effect in molecules and crystals. New York: Wiley-Interscience, 1972
12. Trindle, C.: J. Am. Chem. Soc. **92**, 3251 (1970), J. Am. Chem. Soc., **92**, 3255 (1970)
13. Halevi, E. A. J. Am. Chem. Soc.: Int. J. Quant. Chem., Vol XII, Suppl. **1**, 289 (1977)
14. Bachler, V., Halevi, E. A.: Theoret. Chim. Acta (Berl.) **59**, 595 (1981)
15. Wilson Jr., C. W., Goddard III, W. A.: J. Chem. Phys. **51**, 716 (1969)
16. Rubinstein, M., Shavitt, I.: J. Chem. Phys. **51**, 2014 (1969)
17. Silver, D. M., Stevens, R. M.: J. Chem. Phys. **59**, 3378 (1973); a) See in particular Figs. 8 and 9
18. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
19. Lathan, W. A., Curtiss, L. A., Hehre, W. J., Lisle, J. B., Pople, J. A.: Progr. Phys. Org. Chem. **11**, 175 (1974), Tab. 3, p. 205
20. Hoffmann, R.: J. Chem. Phys. **49**, 3739 (1968)
    Gimarc, B. M.: J. Chem. Phys. **53**, 1623 (1970)
21. See for example: Kutzelnigg, W.: Einführung in die Theoretische Chemie. Anhang 7.5, Weinheim/Bergstr.: Verlag Chemie, 1975
22. Hylleraas, E. A., Undheim, B.: Z. Physik **65**, 759 (1930)
    MacDonald, J. K. L.: Phys. Rev. **43**, 830 (1933)

Received December 12, 1982