

The Optimum Orbitals for the $H_2 + D \rightleftharpoons H + HD$ Exchange Reaction*

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Abstract

An initio calculations of the optimum generalized self-consistent field orbitals of H_2D have been carried out at various points along the reaction path for the three-center exchange reaction, $H_2 + D \rightleftharpoons H + HD$. The emphasis here is on a qualitative interpretation of the changes in these orbitals during the reaction.

In order to fully understand the factors affecting a chemical reaction, it is important to have a clear idea of how the bonding states change and distort during the reaction. In order to abstract from the wavefunction conceptually useful information concerning the states of the molecule, it is important to consider wavefunctions allowing an independent particle interpretation. The method we use yields essentially the best wavefunction which can be interpreted in terms of N independent spatial orbitals [1] (for N electrons) and can be considered a generalization of the valence bond and Hartree-Fock methods in which no restrictions are made on the forms of the orbitals, no orthogonality conditions are imposed, and both the orbitals and the spin coupling are optimized [1]. This method is just the modification of the GI method [2] in which the representation of the symmetric group is optimized; for this reason it is called the spin-coupling optimized GI or SOGI method [1].|| Since this method yields essentially the best independent particle wavefunctions, it should be appropriate for the study of chemical reactions. Here we will consider the simple $H_2 + D \rightleftharpoons H + HD$ exchange reaction, which forms a prototype for a general class of hydrogen atom transfer reactions, $AH + B \rightleftharpoons A + HB$. The emphasis here is on the orbitals and a qualitative interpretation of how they change during the reaction.

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|| For a review and further discussion of this and related methods for electronic wavefunctions, see the discussions by P. O. Löwdin and W. A. Goddard III elsewhere in this Symposium [3].

These calculations used a basis set of two *s*-like and one *p*-like Slater functions on each center. The geometries for the points on the reaction path were taken from the configuration interaction (ci) calculations by Shavitt and coworkers [4] as were the orbital exponents for the basis functions. We will consider only points on the reaction path (linear).

We consider the H₂ at the left and label the centers A, B, and C from left to right. At infinite separation between H₂ and D, orbital ϕ_3 is exactly the orbital for D and orbitals ϕ_1 and ϕ_2 are exactly the orbitals for H₂, the ϕ_1 more concentrated on A and ϕ_2 more concentrated on B [2]. As the internuclear distance R_{BC} is decreased, but still kept large, ϕ_1 and ϕ_2 each build up some extra amplitude on center C (see Figure 1a). In the region of C, ϕ_2 has nearly the same shape as it would have in the case of H₂ (BC) where center A is deleted; that is, near C the orbital ϕ_2 has bonding character. Similarly, ϕ_1 has bonding character near C. On the other hand, ϕ_3 although nearly a pure hydrogen orbital on D, has a node between A and B. Thus for finite R_{BC} the energy of ϕ_3 should be greater than the energy for $R_{BC} = \infty$, and we say that ϕ_3 is slightly antibonding. The energy increase due to ϕ_3 would be decreased by increasing R_{AB} * and hence we expect R_{AB} to increase as R_{BC} decreases. The net result of ϕ_1 and ϕ_2 bonding H₂ to D and ϕ_3 antibonding D to H₂ is a slight increase in energy as R_{BC} decreases.

A further decrease of R_{BC} leads to a further increase of R_{AB} and a magnification of the above tendencies (see Figure 1b). Orbital ϕ_2 becomes more strongly bonded to C and less so to A, and ϕ_1 becomes more concentrated on C at the expense of A and exhibits an increase of bonding between B and C and a decrease of bonding between A and B. The net result of these changes is some increase in bonding. However in response to the above changes, ϕ_3 shifts somewhat from C to A, becoming significantly negative on C. Thus ϕ_3 becomes even more antibonding between A and B.

As we approach the transition state, ϕ_2 and ϕ_1 shift more and more amplitude from A to C so that in the transition state the orbitals are symmetric (i.e., σ_g) orbitals (see Figure 1c). In response to these changes ϕ_3 shifts amplitude from C to A and gradually moves the nodal plane to B. Thus in the transition state ϕ_3 is an antisymmetric (i.e., σ_u) orbital.

From these calculations we obtain a barrier height of 17 kcal/mole as compared to 11 kcal/mole from the best current configuration interaction (ci) calculations [4]. This larger value for the activation energy as compared to the ci value can be viewed as due to a change in the dynamic correlation of the electrons as we move from having two electrons in the same region at $R_{BC} = \infty$ to having three electrons in the same region at the transition state.

As we pass through the transition state toward H + HD, we see that ϕ_1 and ϕ_2 continue transferring amplitude from A to C with ϕ_1 eventually becoming

* We have in mind here optimizing R_{AB} with, say R_{BC} kept fixed, as we might do in determining the reaction path. Orbital ϕ_3 favors an increase of R_{AB} but this is opposed by ϕ_1 and ϕ_2 ; the resulting R_{AB} is a compromise, but should increase as R_{BC} decreases.

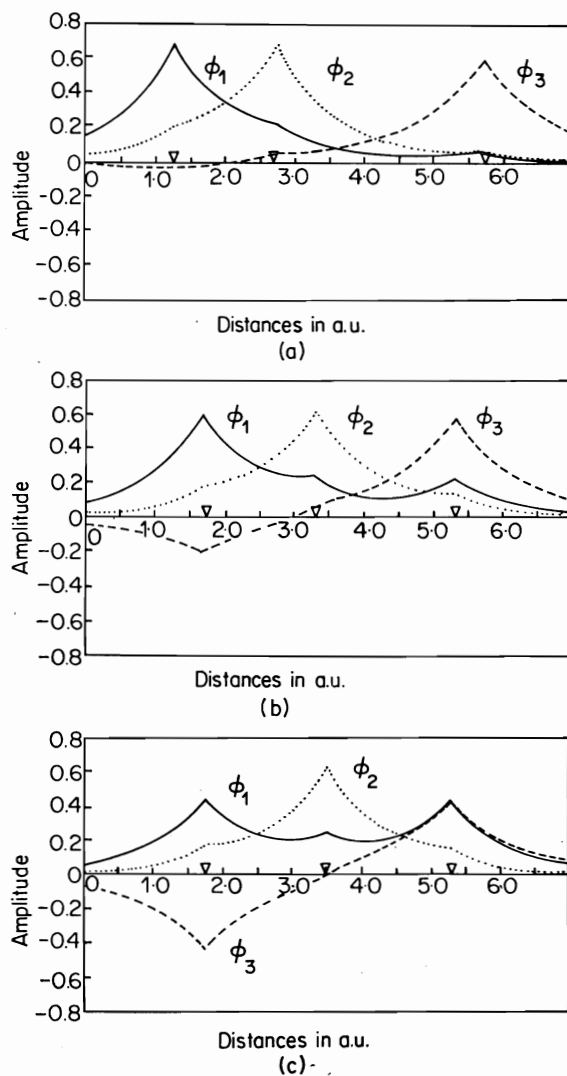


Figure 1. The optimum orbitals for the $\text{H}_2 + \text{D} \rightleftharpoons \text{H} + \text{HD}$ exchange reaction. Each point is for a linear configuration along the reaction path, the centers are denoted as A, B, and C, from left to right. (a) $R_{\text{AB}} = 1.470$, $R_{\text{BC}} = 2.984$, energy = -1.6422 ; (b) $R_{\text{AB}} = 1.609$, $R_{\text{BC}} = 2.020$, energy = -1.6263 ; (c) $R_{\text{AB}} = 1.765$, $R_{\text{BC}} = 1.765$, energy = -1.6238 ; for $R_{\text{AB}} = 1.4$ and $R_{\text{BC}} = \infty$, the energy is -1.6515 .

localized on C while ϕ_2 remains most localized on B. Correspondingly, ϕ_3 becomes more concentrated on A with the node moving between B and C. Thus in the limit of $R_{AB} = \infty$, ϕ_2 and ϕ_1 are pure HD orbitals on B and C and ϕ_3 is a pure H orbital on A. It is interesting to note here that in the exchange reaction, the orbitals of the outside atoms (A and C) actually do exchange, with ϕ_1 going from A to C and ϕ_3 from C to A.

From an examination of Figure 1, we see that in this three-center exchange reaction, the three orbitals gradually delocalize over all three atoms and then relocalize again to form the product states. Two of the orbitals become more bonding and one becomes somewhat antibonding so that the net result is an increase in energy far less than the bond energy of the H_2 .

Thus these calculations provide an *a priori* quantum mechanical orbital picture of the concerted reaction mechanism (the breaking of the old bond is aided by the simultaneous formation of the new one), which has been successfully used for many years. We would expect this orbital behavior to be typical of hydrogen atom transfer reactions for larger systems, except that if A and B are not symmetrically related, the transition state orbitals would not have *g* or *u* symmetry.

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