

## Limits of the concept of reactivity

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In spite of the usefulness of concepts related to reactivity, finding of a universally applicable recipe is hampered by the very nature of the problem, reactants behave differently under the influence of different reactants. Key elements in producing this diversity are degeneracy, and the irrelevance of asymptotic behavior for understanding equilibrium points on the potential energy surface. Simple examples are given to illustrate it.

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The idea of reactivity starts from the desire to know how an electronic system reacts without having to specify the system with which it reacts. Unfortunately, there are intrinsic limitations to such a concept that can be related to the complexity of quantum mechanics which has to be taken into account when describing electronic systems. Depending on the partners with which the system of interest interacts, the reactivity measures can become ill-defined or even useless. Introducing reactivity concepts specific to certain classes of reactions certainly can reduce this problem. Unfortunately, we still do not have a general classification of reactions that would always allow to predict how an arbitrary system behaves.

The present paper presents some situations where the concept of reactivity can become problematic. They can be loosely classified into two groups. The first group of limitations shows up because degeneracies are present. In such a case, characterizing one of the members of the degenerate states may be useful for one reaction, and misleading for another. (Taking the ensemble average of the degenerate states, may make it useless for both). The second group of limitations shows up even when degeneracy is lifted, and we study the chemical reaction as a perturbation of the reactants.

No specific reactivity indicator is analyzed below. It is shown that an important variation of the state of the system, its density or spin-density, is significant enough to make us abandon the aim to find a single, significant reactivity indicator.

In order not to add to the confusion, effects solely due to approximations will not be considered in this paper.

### Effect of Degeneracy

When degeneracy is present for the system under study (e.g., because it is an open shell system), or among reactants (e.g.,  $X...X^+$  is degenerate with  $X^+...X$ ), the total wave function at infinite separation between the reactants (A and B) can be written as a linear combination of the degenerate states (Eq. 1).

$$\Psi_{AB} = \sum_{a(\text{on } A)} \sum_{b(\text{on } B)} c_{ab} \Psi_a \Psi_b \quad \dots (1)$$

$\Psi_a$ , and  $\Psi_b$  are both anti-symmetric, but their product need not be antisymmetrized as expectation values do not change by anti-symmetrization, due to the infinite separation of A and B. A slight perturbation or a weak interaction between the fragments can select a possible state among the possible ones. In such a case, reactivity indicators will vary over a certain range<sup>1-3</sup>, that can be large. Maybe the simplest example is given by  $H_2^+$  where the electron density of one of the centers can vary between zero and that of a hydrogen atom ( $H^+...H$  to  $H...H^+$  passing through  $H^{+1/2}...H^{1/2}$ ). A very weak field can shift charge from one atom to another. Using an indicator, e.g., related to the ionization potential of the H atom makes little sense for this kind of charge transfer.

Another simple example is provided by three H atoms at infinite separation, arranged on the corners

of an equilateral triangle. The unpaired electron can be on any of the degenerate states, so that both the density and the spin-density can vary for a slight deformation from the geometry of the equilateral triangle.

Such phenomena can appear also for closed shells. A simple (but admittedly unrealistic) example is that of a  $H^-$  ion, and an  $\alpha$  particle ( $He^{2+}$ ). The moment the fragments interact, it is not a ground state anymore. To get into the ground state, both electrons are transferred from H to He, the energy of  $H^-$  ( $\approx -0.53$ ) or that of H and  $He^+$  ( $= -2.5$ ) being higher than that of He ( $\approx -2.90$ ). Using, for example, an indicator based upon the electron density of  $H^-$  as a reactivity indicator is useless.

Taking ensemble quantities can deform the picture. A well-studied example is the deformation density in the  $F_2$  molecule, where using oriented atom densities as reference correctly gives a density accumulation between atoms, while sphericalized atomic densities do not (see, e.g., Fig. 1 of Ref. 4).

### Irrelevance of Asymptotic Behavior

A seemingly natural viewpoint to restrict the degrees of freedom of the system under study is to consider it as perturbed by the other reactants. For example, it is natural to provide quantities like the density-density linear response function  $\chi(r, r')$ , from which we can extract the density change of the subsystem of interest,  $\delta\rho(r)$  for an arbitrary change due to the change in the potential of other reactants,  $\delta v(r)$  (Eq. 2).

$$\delta\rho(r) = \int d^3r' \chi(r, r') \delta v(r') \quad \dots (2)$$

Is the behavior at large internuclear separations relevant for the behavior at shorter, “chemical bond” distances? The answer is not always positive. Take for example the primitive case of the hydrogen molecule in the lowest triplet state,  $b^3\Sigma_u^+$ . Although the potential energy curve is mostly repulsive, at large interatomic distances, it presents a van der Waals minimum<sup>5</sup> see (Fig. 1). Thus, the way two triplet-coupled H atoms interact at large internuclear separations (binding) is not relevant for the behavior at shorter distances (repulsive).

One may argue that in this example, the state chosen is not that of the lowest energy. Although it would be sufficient to say that when discussing reactivity we should be able to describe repulsive states too, let us counter-argue by considering another example. The  $F_2$  molecule that at equilibrium distance has a ground

state of  $^1\Sigma_g^+$  symmetry, Figure 8 of Ref. 6 shows that for large internuclear separations, two  $^3\Pi_u$  adiabatic states lie below the  $^1\Sigma_g^+$  one. The explanation given is that in  $^3\Pi_u$  states the wave function allows a long range attractive interaction of the quadrupoles of the two atoms, while in the case of the  $^1\Sigma_g^+$  the alignment of the quadrupoles is repulsive. The lowest energy state at large interatomic distances that one would have selected by analyzing two perturbed F atoms is not related to the ground state of the  $F_2$  molecule.

One may further argue that, in the preceding example one could distinguish between singlet and triplet states. A counter-example is given by the  $C_2$  molecule. Until very close to the equilibrium distance, the lowest energy state is of  $^1\Delta_g$  symmetry, and not  $^1\Sigma_g^+$ , as at the equilibrium distance (cf. Fig. 1 of Ref. 7).

Finally, one may argue that the  $C_2$  molecule is exotic. However, there are well known systems that are predominantly ionic at equilibrium, and are neutral when separated (e.g., ionic crystals). Thus, considering a perturbation far from the point of interest on the potential energy surface may be misleading.

### A Combined Example

As a last example, let us consider again a system that can be produced by quantum mechanical entanglement. We consider four spin-1/2 systems, aligned infinitely far apart, labeled from A to D. Let us consider the wave functions for which (initially) both the pair A and B and the pair of atoms C and D are coupled to a singlet. To start with, we do not consider any interaction between the AB and the CD pair. Let us now perturb the system, by coupling systems B and C and analyze the system we have produced. If, by this, the pair BC forms a singlet, the atoms A and D are also coupled to a

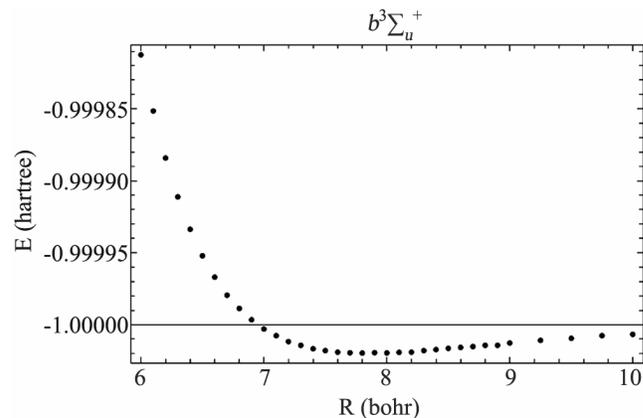


Fig. 1—Energy of the  $H_2$  molecule in the  $b^3\Sigma_u^+$  state (data from Ref. 5).

singlet although we did not suppose any interaction between A and D. Please notice that we could have coupled B and C to a triplet, and obtain a triplet coupled A and D. The example presented may seem exotic, but it not only has been an object of entanglement experiments (see Refs 8 and 9), but is also an elementary example for valence bond coupling schemes.

### Conclusions

Although the concept of reactivity has proven its usefulness over many years, traps exist. Their origin lies in the diversity of electronic states that can be produced, and their quantum nature.

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