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Comment on ‘Potential energy surfaces of excited states of H_2^-’ (Chem. Phys. Lett. 285 (1998) 114–120)

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Abstract

The H_2^- excited state potential curves of Mebel et al. (Chem. Phys. Lett. 285 (1998) 114–120) are re-analysed. They are shown to be artefacts of the method of computation, with little or no relation to real states. The need for caution in the use of bound state electronic structure methods to study resonance parameters is re-emphasized. © 1999 Elsevier Science B.V. All rights reserved.

In a recent Letter, Mebel et al. [1] report a calculation of the potential energy curves of excited states of H_2^-, using a multi-reference configuration interaction approach (MRCI). In the case of negative molecular ions, we assert that it is dangerous to use this approach without safeguards since any states produced this way are likely to bear little or no relation to ‘real’ (i.e. experimentally realizable) states. In this Comment, we show explicitly that this is the case with the results of Mebel et al., with the aim of discouraging any future use of this method in the calculation of negative molecular ions.

Except for the ground state at long bond length, all states of H_2^- are unbound. They can therefore be seen experimentally only as temporary pseudo-states or resonances produced through the interaction of an electron with H_2. Mebel et al. state that ‘‘electron impact experiments on hydrogen might show strong resonances’’. In fact, there is a long history of electron–H_2 scattering experiments dating back over 30 years which have set out directly to study these resonances using a variety of different methods [2–14]. Work in this area has continued, but experimental work on H_2^- resonances was comprehensively and cogently reviewed as long ago as 1973 by Schulz [15] and more recently by Trajmar et al. [16].

Although historically there has been little agreement on the assignment of the resonances seen, there has been excellent agreement about the energy positions of the resonance states which are each seen as a vibrational series. The most comprehensive experiment was that of Comer and Read [5] who produced potential curves from their results which could be compared directly with theoretical predictions. Alongside the experimental work is a large body of theoretical calculations which can be split broadly into two groups: electronic structure calculations

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[1,17–25] and scattering calculations [26–33]. Within the electronic structure calculations, we would draw distinction between stabilization calculations [17–21], which make explicit allowance for continuum effects and in most cases appear reliable, and more recent calculations based on pure bound state methodologies [1,22–25]. It is the pure bound state methods, the most recent of which is due to Mebel et al., we address here.

The most comprehensive scattering calculation on H_2^- resonance states was recently reported by us [32,33]. In this work, we found all of the low-lying resonances that had been seen experimentally and satisfactorily resolved all the ambiguities over their assignment. In particular, we were able to demonstrate that many of the difficulties encountered by experimentalists in attempting to assign resonances was caused by the incorrect assumption that each resonance must be associated with a single 'parent' electronic excited state of H_2. Comparing with both experimental results and our results, we find that in nearly all cases, the published electronic structure calculations [1,22–24] produce spurious resonances with no connection with experiment, alongside a genuine (at least at some bond lengths) resonance or resonances. This can cause much confusion when comparing experiment with theory. For instance, a calculation by Eliezer et al. [19], despite including some degree of stabilization, produced a spurious $^2\Sigma_g^+$ symmetry resonance. Mason and Newell [13] and Furlong and Newell [14] found 'good agreement' between their experimental 'series *c*' resonance, which is actually of $^2\Pi_u$ symmetry, and the spurious $^2\Sigma_g^+$ resonance.

Except for the ground $X^2\Sigma_u^+$ state, there is no agreement between any of the Mebel et al. H_2^- states and observed experimental states. There is also no agreement between their states and any states found through the scattering calculations, which generally agree with experiment. Again, except for the ground state, there is little or no agreement between the results of Mebel et al. and the other electronic structure calculations, or among the other electronic structure calculations. The suggestion of Mebel et al. of a favourable comparison between their *fourth* $^2\Sigma_u^+$ state and the *second* state of DeRose et al. [23] is misleading. The curves are 1.8 eV apart and their minima are not significantly close. With so many spurious potential curves, it is not surprising that sometimes curves from different calculations lie close together, but this cannot be taken as a corroboration.

The reason why these calculations are unreliable is precisely due to the variational collapse which Mebel et al. warn against early in their Letter. Since a negative molecular ion is unbound, an energy-minimizing variational calculation will result in the wavefunction simply collapsing to a 'neutral molecule plus free electron' (NMFE) state. This is approximately equivalent to the H_2 ground state with an electron in the H_2 continuum. Mebel et al. argued that previous calculations attempting to use this method, such as that of Bauschlicher [24], fell into this trap, resulting in a 'crude approximation to the energy continuum of H_2 in the presence of a scattering electron with varying amounts of kinetic energy'. To try and avoid this fate, Mebel et al. tried to constrain the variational calculation by not including any continuum functions or any other diffuse basis functions, citing the valence-bond calculation of McWeeny [25] for justification. Ironically, McWeeny in fact explicitly included diffuse functions in his basis, saying that he would not be able to represent the H_2^- bound state (or by implication the resonance) correctly without them.

The avoidance of particular, diffuse basis functions can be used successfully to prevent calculations of valence states of molecules collapsing into a Rydberg state. However, this works because, by their nature, Rydberg states can be very well described by a single diffuse function. The same, again by its nature, cannot be said for the continuum. In fact, avoiding explicit continuum functions will result in an extremely poor, but still accessible, representation of the continuum through the tails of inner shell functions. Thus the calculation will continue to suffer from variational collapse, only this time it will collapse to a very poor representation of a 'crude approximation to the energy continuum of H_2'.

The calculation by Mebel et al. is similar to the first part of a calculation by DeRose et al. [22] who used a CI calculation to find the first fifteen states of the negative ion system. DeRose et al. stated ''at energies near the resonance there will be several adiabatic states, each of which corresponds to a linear combination of the diabatic resonance plus several diabatic NMFE states. The fundamental problem is to project the diabatic resonances out of the set of adiabatic states.'' DeRose et al. took their states and used a Feshbach projection-operator technique to try to find the resonances. Even this technique only successfully managed to find the ground state and again produced spurious resonances. Mebel et al. have found the adiabatic states with no attempt to project out the resonances, believing the calculation immune from NMFE states.

Alongside the lack of experimental verification, compelling evidence that the states are spurious can be seen by plotting the states $^2\Sigma_g^+$ of Mebel et al. (their figure 2c) along with our results for the H_2^- $^2\Sigma_g^+$ dissociative resonance (see Fig. 1). In the commonly used stabilization method [15], CI H_2^- states (linear combinations of a diabatic resonance plus adiabatic NMFE states) are found in a calculation incorporating a parameter, such as the basis set, that can be varied. By increasing the size of the basis set, diabatic NMFE states will drop in energy whereas the diabatic resonance state should stay at constant energy. Hazi and Taylor [34] used this method to study a one-dimensional model resonance system for which the correct resonance energies were known from a separate scattering calculation. The system was described by N basis functions with the energies and wavefunctions found by diagonalizing the $N \times N$ Hamiltonian. As DeRose et al. [22] described it, ''For small N, the ground state of the system corresponded to the resonance, but as N increased, the ground state dropped sharply in energy and the second state then resembled the resonance. At still larger N, the pattern repeated, and the third state became the resonance. Since the states have the same symmetry, a plot of the energies against N obeys the non-crossing rule.'' In the molecular case here, the quantity being varied is not the number of basis functions, but the bond length. This is an analogous variation as changing the bond length affects the efficiency with which the basis functions can span the relevant space. There is an H_2^- $^2\Sigma_g^+$ resonance, well known both theoretically and experimentally [19–21,35,36], that follows the dissociative $b\,^3\Sigma_u^+$ curve of H_2 before cutting the ground state H_2 and becoming bound. This (diabatic) resonance can clearly be seen in the adiabatic curves of Mebel et al. and, given the limitations on the size and character of their basis, follows our own (scattering) calcula-

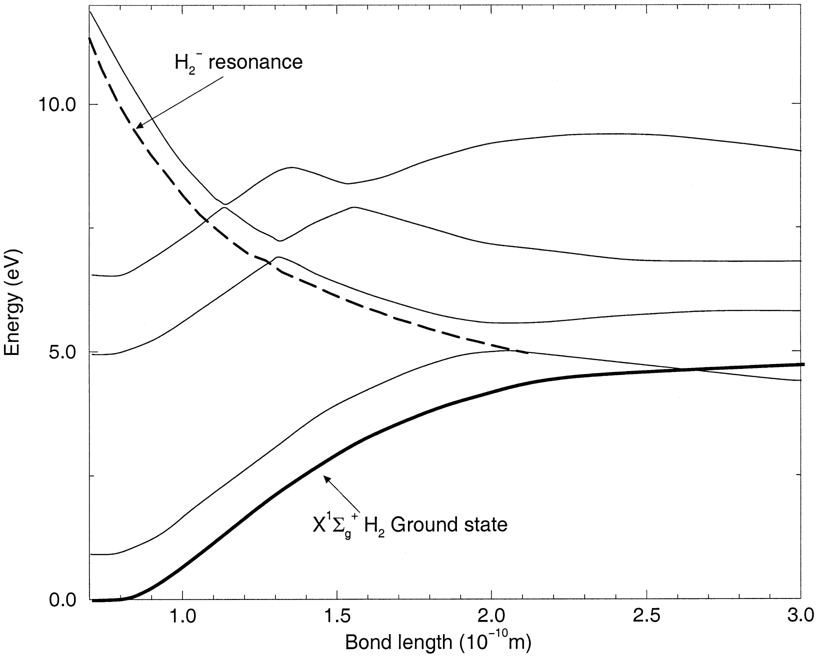

Fig. 1. $^2\Sigma_g^+$ H_2^- potential energy curves of Mebel et al. (thin lines) along with our H_2^- resonance [33] (thick dashed) and the H_2 ground state (thick).

tion of the dissociative resonance [33] remarkably closely (see Fig. 1). The description above of the Hazi and Taylor system in which the resonance moves up the adiabatic curves with increasing *N*, would also perfectly describe the system here as the bond length decreases. In addition it can be seen that most of the spurious curves simply follow H_2 ground state potential, as would expected of a NMFE state.

The $X^2\Sigma_u^+$ H_2^- ground state (well known experimentally in low energy dissociative attachment [36] and theoretically [19,37,33]) is, however, well described by both Mebel et al. [1] and McWeeny [25], but not by Bauschlicher [24]. McWeeny's paper expresses a certain puzzlement over this success and proposes various explanations. Two of these appear important when considering the results of Mebel et al. Firstly, the ground state, as it is described by a relatively small basis in the successful calculations, may have a negligible overlap with the (badly represented) continuum and so can successfully avoid collapsing into a lower NMFE state. Secondly, as there are no other adiabatic resonance-plus-NMFE states in the area, the H_2^- state may prove a good description of the resonance across a range of bond lengths without running into avoided crossings. However, both these situations could easily change with a change of basis, and, without experimental verification, the results are unreliable.

It is clear that the exclusion of continuum and other diffuse functions from the basis is not a sufficient guard against variational collapse in the case of MRCI calculations of H_2^- states. Instead, meaningless superpositions of resonance plus NMFE states are found from which it is difficult to extract the resonance information. This situation would get worse as the size of the molecule increased, as more diffuse orbitals would be required for reasonable representation of the molecule and the continuum would inadvertently be better and better represented. This practice is clearly to be avoided. One possible alternative method would be be the careful use of stabilization.

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