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LETTER TO THE EDITOR

Parent state swapping of resonances in electron–hydrogen molecule scattering

Darian T Stibbe†‡ and Jonathan Tennyson†

† Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
‡ Institute for Theoretical Atomic and Molecular Physics, Harvard–Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138, USA

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Abstract. *Ab initio R*-matrix scattering calculations are presented for electron–H_2 as a function of H_2 bond length. It is found that $^2\Sigma_u^+$ and $^2\Pi_u$ resonances in the 10 eV region appear to be associated with multiple 'parent' target states and that the resonances can swap parents as a function of internuclear separation. It is shown how these phenomena provide an explanation for the inconsistencies in previous assignments of resonances in this region and other anomalies such as pronounced isotopic effects. It is suggested that this parent swapping behaviour is likely to be a common feature of electron-impact excitation of other molecules and is particularly important for any models that include nuclear motion.

The interaction of electrons with molecules underlies our understanding of many natural processes and the development of many technologies. One of the most important processes is electron-impact electronic excitation which is well known to proceed substantially via long-lived quasi-bound or resonant states of the target molecule plus electron system. In many cases these resonances are found to follow closely the potential energy curve of a particular excited state of the molecular target and it is common to assign this as the 'parent state' of the resonance [1]. In this model, the scattering electron is trapped in a potential associated with just this 'parent' state. It is usual for experimental data, such as vibrational series features in differential cross sections, to be interpreted with this assumption.

In the case of electron collisions with the simplest neutral molecule, H_2, analysis of the resonances in the 10–15 eV region has long proven to be problematic. In this energy region there is a bunching of excited target states and corresponding resonances. This has resulted in inconsistencies and uncertainties in assignments [1].

In this work we study resonance states of H_2^- as a function of bond length in order to try to resolve these inconsistencies. These calculations were performed as a prelude to a full treatment including nuclear motion. However, the calculations strongly suggest that the single parent model of these resonances is not valid. It is this aspect of the work we report here.

R-matrix scattering calculations were performed using the UK Molecular *R*-matrix suite of programs [2]. The calculations extend and improve on the H_2 equilibrium geometry studies of Branchett, Tennyson and Morgan [3, 4]. The orbital basis used to obtain the full CI representation of the the seven lowest states of the H_2 target (X $^1\Sigma_g^+$, b $^3\Sigma_u^+$, a $^3\Sigma_g^+$, c $^3\Pi_u$, B $^1\Sigma_u^+$, E, F $^1\Sigma_g^+$ and C $^1\Pi_u$) used in the close-coupling expansion, and the numerical

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orbitals used for the continuum electron were both extended and reoptimized. Fixed-nuclei calculations were performed for bond lengths from $R = 0.8$–$4.0\ a_0$ in steps of $0.1\ a_0$. Further details can be found in [5].

For each symmetry and bond length, resonances were detected automatically and parametrized using the Q-matrix method [5, 6], which fits the time delay as a Lorentzian and/or using the program RESON [7] which fits eigenphase sums to the standard Breit–Wigner form. In both cases these idealized forms are greatly distorted when the resonance lies close to a threshold. However, the Q-matrix method has the advantage that it removes much of the effects of sharply varying backgrounds that are common in multichannel molecular problems.

For ${}^2\Sigma_u^+$ symmetry we found three resonances: the well known, broad $1\sigma_g^2 1\sigma_u$ shape resonance for which there was evidence at low bond length but was only fittable from $R = 1.4\ a_0$ until it becomes a bound state at $R \sim 2.9\ a_0$; a resonance which is fittable for $R < 1.4\ a_0$ (and is weakly apparent at longer bond lengths) which closely tracks its parent, the b ${}^3\Sigma_u^+$ state and a higher resonance which we detect for all R. The higher two resonances are shown in figure 1 along with the H_2 target state potential energy curves relative to the ground state. It can be seen that the higher resonance starts off following the a ${}^3\Sigma_g^+$ target state but then in the region of $R = 1.7\ a_0$ swaps over to the B ${}^1\Sigma_u^+$ state.

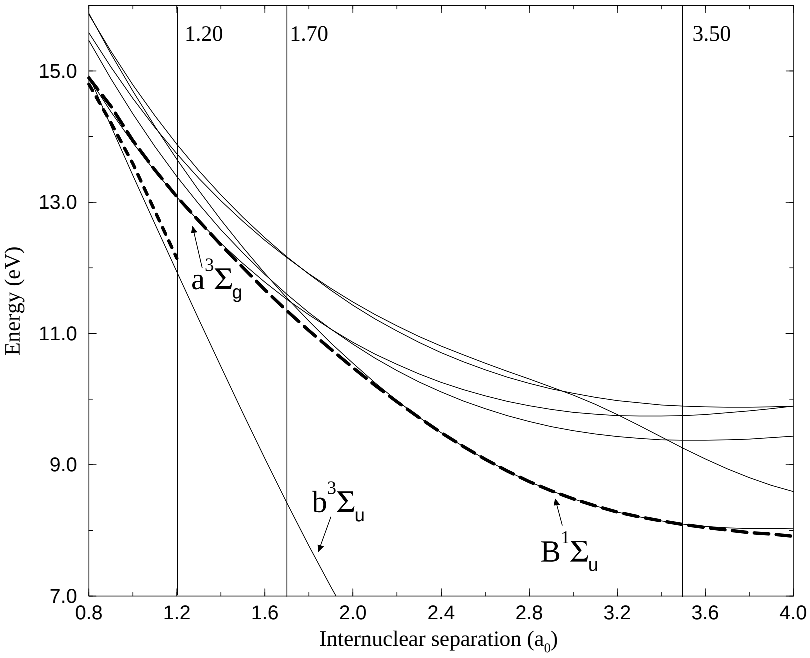

Figure 1. ${}^2\Sigma_u^+$ total symmetry resonances (thick broken curves) as a function of bond length, with target thresholds relative to the ground state. Only the higher two resonances found in this work are shown.

A similar phenomenon is encountered for ${}^2\Pi_u$ total symmetry, for which we only detect one resonance. Figure 2 shows that this resonance follows the a ${}^3\Sigma_g^+$ state for $R < 1.7\ a_0$, swaps to the c ${}^3\Pi_u$ state before swapping again and settling on the E, F ${}^1\Sigma_g^+$ for $R \geqslant 3.5\ a_0$. These results are very interesting when compared with experimental results for this *series c* [1] resonance. Comer and Read [8] could not decide between the c ${}^3\Pi_u$ and the a ${}^3\Sigma_g^+$

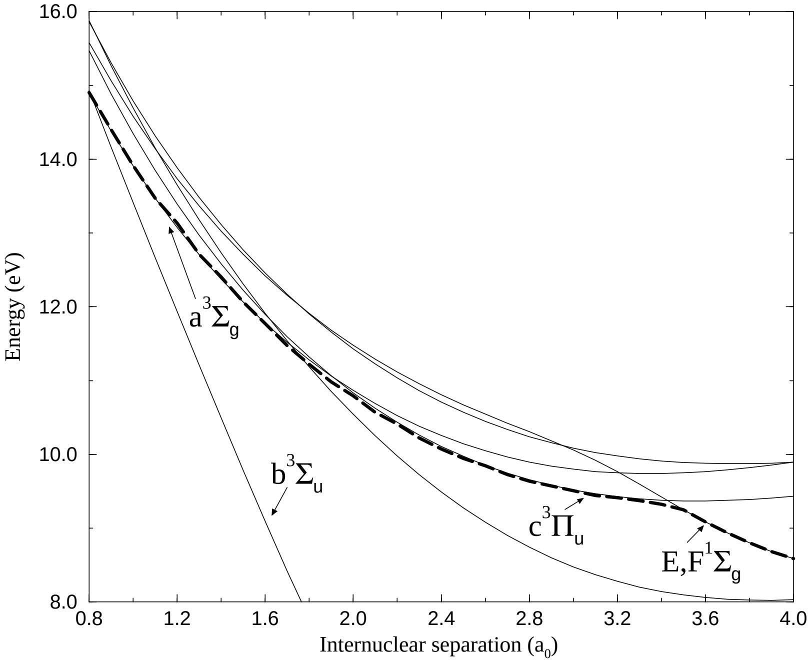

Figure 2. The $^2\Pi_u$ total symmetry resonance (thick dotted curves) as a function of bond length, with target thresholds relative to the ground state.

as parents when looking at D_2. Mason and Newell [9], when looking at this resonance in H_2, took the parent to be the c $^3\Pi_u$ state in agreement with what they called the accepted designation.

Both the $^2\Sigma_u^+$ and $^2\Pi_u$ resonances upon which we focus remain 0.2 eV or less below a target threshold for all R. Under these circumstances it is hard to determine the resonance widths to high accuracy. However, fits were performed to those portions of the Lorentzians given by the time-delay method which are relatively unperturbed by the threshold. At short R, the upper $^2\Sigma_u^+$ resonance interacts with the lower resonance. It starts off with a narrow width which rises to a maximum of $\Gamma \sim 0.03$ eV at $R = 1.1$ a_0, decays quasi-exponentially between $R = 1.1$ and 2.0 a_0, and is nearly constant at 0.002 eV for $R > 2.0$ a_0. The $^2\Pi_u$ resonance width rises slowly from around 0.03 eV at $R = 0.8$–0.08 eV at $R = 1.2$ a_0 before dropping rapidly to 0.005 eV at 1.5 a_0, from where it is nearly constant until it begins to rise steeply again at $R > 3.0$ a_0. In both cases the widths change a great deal at approximately the positions where the resonances appear to swap parents.

Analysis of the inner region to help determine parenthood can be performed by plotting a resonance along with the R-matrix poles (inner region compound system eigenvalues). It is sometimes possible to correlate the resonance with one particular pole and hence identify it with a target plus continuum configuration. Here, any attempt to do this was thwarted by the high density of interacting poles in the region of the resonance which meant it was impossible to identify the resonance with one pole. Analysis of the partial waves of the scattering electron in the outer region can be done either by looking at the eigenphases of each channel or at the time-delay eigenvector. However, this also will not work in this case as the resonance lies below the possible parents and so those channels are closed.

For both total symmetries, since there is no second resonance in the vicinity, an avoided curve crossing is not a possible explanation for the observed parent swapping. The explanation proposed here is that each resonance is actually associated with multiple target states, i.e. that the potential in which the electron is temporarily trapped is made up of contributions from a number of target states. At a particular bond length, it is possible that one parent (in both the cases studied here, the lowest in energy) dominates and the resonance is largely associated with that state (the dominant parent would have custody with the other parents allowed limited visiting rights). However, as the bond length is varied and particularly if target states cross, the relative importance of each of the parent target states changes so that another target state becomes dominant. Thus the resonance appears to swap parents as the bond length is varied.

Previous multi-state electron–H_2 scattering calculations performed at a single bond length would simply assign any resonance seen to an apparently single-parent target state, the dominant parent at that particular bond length.

In order to confirm the multi-parent hypothesis, reduced-state calculations are performed, here concentrating on the simpler ${}^2\Sigma_u^+$ symmetry. The target states that dominate across the range of bond lengths are the a ${}^3\Sigma_g^+$ and the B ${}^1\Sigma_u^+$ and those are the ones included in the calculations, although other target states might also be part of the interaction. When performing these reduced-state calculations, it is necessary also to include the b ${}^3\Sigma_u^+$ state as its omission results in the disappearance of the middle ${}^2\Sigma_u^+$ resonance and consequently produces spurious resonance-like features in the time delay.

The following reduced-state calculations are performed at several bond lengths: (i) X ${}^1\Sigma_g^+$, b ${}^3\Sigma_u^+$ and a ${}^3\Sigma_g^+$ 'three-state/a ${}^3\Sigma_g^+$'); (ii) X ${}^1\Sigma_g^+$, b ${}^3\Sigma_u^+$ and B ${}^1\Sigma_u^+$ ('three-state/B ${}^1\Sigma_u^+$') and (iii) X ${}^1\Sigma_g^+$, b ${}^3\Sigma_u^+$, a ${}^3\Sigma_g^+$ and B ${}^1\Sigma_u^+$ (the 'four-state').

Figure 3 shows the results of the reduced and seven-state calculations at $R = 1.2\ a_0$ (when the resonance is associated with the a ${}^3\Sigma_g^+$ state), $R = 1.7\ a_0$ (when the resonance is in the process of crossing between states) and $R = 3.5\ a_0$ (when the resonance is associated with the B ${}^1\Sigma_u^+$ state). The figures show plots of the time delay experienced by the scattering electron. The thresholds of the two key target states, a ${}^3\Sigma_g^+$ and B ${}^1\Sigma_u^+$, are labelled and other thresholds from the seven-state calculation are marked. In the time-delay picture, an undistorted resonance will appear as a perfect Lorentzian although a nearby threshold can distort the shape of or cut off a resonance. The time delay at threshold itself should become infinite although this point can be missed due to the coarseness of the grid.

At $R = 1.2\ a_0$, the resonance in the seven-state calculation appears approximately at the a ${}^3\Sigma_g^+$ threshold. The three-state/a ${}^3\Sigma_g^+$ calculation shows little or no sign of resonance. The three-state/B ${}^1\Sigma_u^+$ calculation shows a resonance just above its threshold. With the four-state calculation, this resonance forms a part of a resonance of about double the width of the seven-state resonance at approximately 0.3 eV above it. The decay fractions of the four- and seven-state resonances to the a ${}^3\Sigma_g^+$ state are very similar (0.33 for the seven-state calculation and 0.31 for the four-state) and they are almost certainly the same resonance. The differences in shape and position are due to the additional target states in the seven-state calculation. It is well known that increasing the number of states in a close-coupling calculation pushes down the position of a resonance [4]; usually it also leads to a corresponding narrowing.

At $R = 1.7\ a_0$, the thresholds of the a ${}^3\Sigma_g^+$ and B ${}^1\Sigma_u^+$ cross and the seven-state calculation has a well resolved resonance at around 11.35 eV, approximately 0.2 eV below the crossing energy. The three-state/a ${}^3\Sigma_g^+$ calculation is affected by the threshold but shows no sign of resonance. The three-state/B ${}^1\Sigma_u^+$ calculation shows slight traces of a

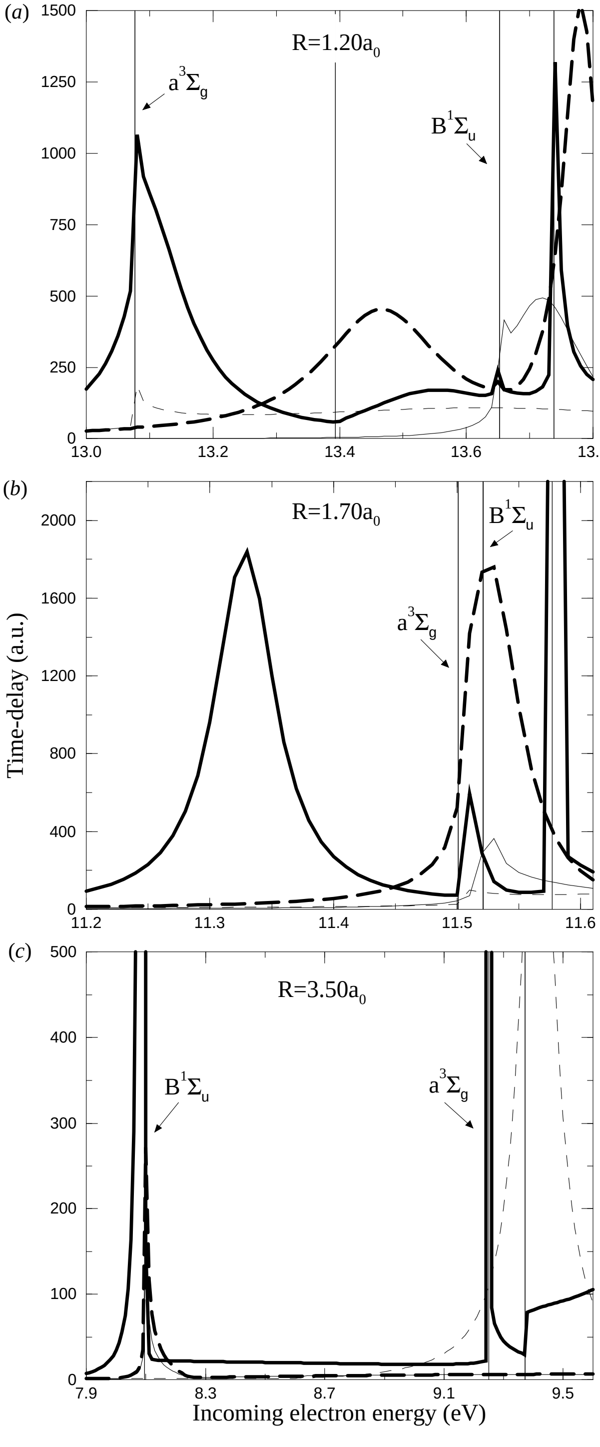

Figure 3. Time delay as a function of electron energy for (i) full seven-state (thick, full) (ii) three-state/a $^3\Sigma_g^+$ (thin, broken); (iii) three-state/B $^1\Sigma_u^+$ (thin, full) and (iv) four-state (thick, broken) at bond lengths of (*a*) $R = 1.2\ a_0$, (*b*) $R = 1.7\ a_0$ and (*c*) $R = 3.5\ a_0$. See text for details.

resonance around the target threshold. When both these states are included in the four-state calculation, a clear resonance is seen at around 11.55 eV, with almost exactly the same shape as the full seven-state resonance but at an energy about 0.2 eV higher. This energy shift can again be explained by the greater number of states in the seven-state calculation.

At $R = 3.5\ a_0$, the a $^3\Sigma_g^+$ threshold is now well above the B $^1\Sigma_u^+$ threshold and in the seven-state calculation, a sharp resonance appears just below the B $^1\Sigma_u^+$ threshold and cut off at higher energies by it. In the three-state/a $^3\Sigma_g^+$ calculation, there is a very clear resonance that appears a little above the a $^3\Sigma_g^+$ threshold. In the three-state/B $^1\Sigma_u^+$ calculation, there is a feature just above threshold that appears to be the tail end of a resonance cut off by the threshold. In the four-state calculation, including both of these states, the three-state/a $^3\Sigma_g^+$ resonance can no longer be seen at its original position. Just above the B $^1\Sigma_u^+$ threshold, the tail-end of a resonance much sharper than the three-state/B $^1\Sigma_u^+$ feature and closer to the one with the seven-state calculation is seen, cut off at lower energy by the threshold.

At all the bond lengths, the resonance seen in the full calculation only appears when both the a $^3\Sigma_g^+$ and B $^1\Sigma_u^+$ states are included. When resonances do appear in the three-state calculations such as in the three-state/a $^3\Sigma_g^+$ at $R = 3.5\ a_0$ or the three-state/B $^1\Sigma_u^+$ at $R = 1.2\ a_0$, then in the four-state calculation they become part of the new resonance. These facts strongly suggest that this new resonance has both those target states as joint parents. At short bond length, the a $^3\Sigma_g^+$ parent state is almost fully dominant. At $R = 1.2\ a_0$ the resonance in the seven-state calculation lies just above its apparent parent, a $^3\Sigma_g^+$. Assuming the single-parent model, the decay fraction to this parent would be expected to be almost 1 but in fact is only 0.33 suggesting that this state is no longer totally dominant. At the equilibrium distance, $R = 1.4\ a_0$, a $^3\Sigma_g^+$ is still dominant, but only just. A previous calculation performed at the fixed equilibrium geometry saw a resonance at this energy but could not fit a resonance using the eigenphase sum method due to a falling background [4]. At the point where the two parents meet in energy (around $R = 1.7\ a_0$), they have approximately joint custody of the resonance. At greater bond length, the B $^1\Sigma_u^+$ state becomes the dominant parent.

The observation that the parentage of particular resonances can be more complicated than the single-parent model has been made before [10] but has seemingly been ignored.

An example of the power of the multi-parent state model can be seen in the *series a* [1] H_2^- resonance which has $^2\Sigma_g$ symmetry. This resonance lies just below a bunch of four target states (c $^3\Pi_u$, C $^1\Pi_u$, a $^3\Sigma_g^+$ and the inner E region of the E, F $^1\Sigma_g^+$) and it is impossible to tell just from the shape of the curve which state it is following. As it lies below the possible parent states, decay fractions cannot help. Eliezer *et al* [11] used a quasi-vibrational method to calculate the potential energy functions of the Σ^+ states of H_2^- and found the lowest in energy to be predominantly c $^3\Pi_u$ + e$^-$. Comer and Read [8] saw the resonance experimentally and following the lead of Eliezer *et al* assigned it to c$^3\Pi_u$. Da Silva *et al* [12] performed a five-state calculation which despite not including any Π states still saw the resonance and assigned it as a $^3\Sigma_g^+$. Stibbe and Tennyson [5] included the Π states and also assigned it to the a $^3\Sigma_g^+$ state although they did note that there was some interaction with the other three states. These apparent inconsistencies are entirely explained by the idea that a resonance can in actual fact have multiple parent states. It is clear that calculations using different methods and including different states and experiments which measure different aspects of the same interaction could easily assign resonances differently if forced to choose a single parent. It is also worth noting that the assumptions often made when fitting vibrational series data, in particular that the resonance width is independent of the internuclear separation and that the pseudostate potential follows a Morse function [8], can clearly fail in the case of a resonance that swaps parents.

Similarly, the difficulties in assigning a parent for the $^2\Pi_u$ resonance are also explained. In the region close to the equilibrium bond length, which is the region mostly sampled by the experiments, the dominant parent of the resonance swaps from a $^3\Sigma_g^+$ to c $^3\Pi_u$. Hence, if again forced artificially to choose one or the other, it is quite possible that different target state parents will be chosen. It is also possible that because the swapping occurs in such a sensitive area, large isotopic effects might occur and indeed this has been seen in the metastable excitation cross sections of the *series c* resonance line for H_2, HD and D_2 [13] and in the relative intensities of the *series a* and *c* lines [14]. Quantative theoretical treatment of this problem will require the explicit inclusion of nuclear motion.

In conclusion, the idea of multiple parents and the possible swapping between parents with bond length provides an explanation for the difficulties previously encountered when trying to assign resonances under the assumption of a single-parent target state. Indeed, it would suggest that a re-examination of previously found or calculated raw data might prove fruitful. Given that parent swapping appears in electron collisions with the most basic, fundamental neutral molecule, H_2, it is likely to be important in electron collisions with larger, more complicated molecules where there can easily be a bunching of target states (although it will not affect the low-energy shape resonances often seen in large molecules) and indeed inconsistencies and difficulties in the assignment of resonances in N_2 and CO electron scattering have been noted previously [14]. This has major consequences, both for any future electron–molecule scattering calculations in which the motion of the nuclei is included and in the interpretation of experimental data.

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