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# Two - centre Electronic Wavefunctions in Plasmas

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Two - centre electronic wave functions

in plasmas

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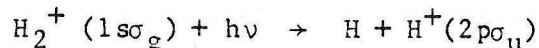
Abstract

The electronic structure occurring during collisions between ions in a plasma is considered in terms of two-centre wave functions and exact solutions of the Schroedinger equation for the  $H_2^+$  molecule are used to describe collisions between H atoms and  $H^+$  ions in a hydrogen plasma. This 'transient chemistry' shows the existence of transitions not accounted for in the usual single-centre treatments and a coupling between radiation and ionic kinetic energy not previously described.

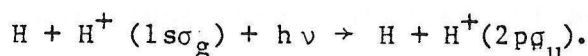
## 1. Introduction

One of two general approaches is usually used in the calculation of the electronic structure of a plasma. The first involves an initial calculation of the electronic structure of an isolated ion. The effect of the surrounding plasma is introduced by perturbation theory. In the second method the effect of the surrounding plasma is included in an initial calculation of a spherically symmetric (such as Thomas-Fermi) potential. The electronic structure is then calculated by solving the electronic wave equation using this potential. Such single-centre calculations are regularly performed to obtain, for example, the radiative opacity of a plasma.

Bates (1952) has investigated the contribution to the radiative opacity of stellar atmospheres arising from absorption by  $H_2^+$  ions

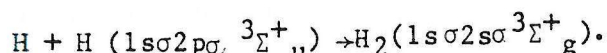


and from the transient molecule formed by colliding H atoms and  $H^+$  ions



Although Bates (1952) calculates the contribution to the stellar opacity from these processes, because of lack of data on the  $H_2^+$  ion, in each case he only considers the transition  $1s\sigma_g \rightarrow 2p\sigma_u$ .

Several authors (Erkovich 1960, Zwaan 1962, Solomon 1964) have considered the contribution to the stellar opacity arising from the absorption of transient molecular hydrogen



However they only consider a bound final molecular state.



Subsequent applications of the concept of transient molecule formation in a plasma has been concerned with the calculation of line shapes and in particular quasi-molecular satellites (e.g. Stewart, Peek and Cooper, 1973).

It is the purpose of the present note to point out that the use of two-centre wave functions to describe the electronic structure of a plasma predicts contributions to plasma properties not existing in the usual single-centre treatment. These contributions may be described as arising from the 'transient chemistry' of the plasma.

## 2. Transient $H_2^+$ formation in a hydrogen plasma

As in the work of Bates (1952) this note assumes the validity of the Born-Oppenheimer approximation which allows the solution of the electronic wave equation at fixed nuclear separations; the nuclear equation of motion involving the potential energy surface obtained. To be of most use in this application, the two-centre electronic wavefunctions must be known accurately. The molecule for which the most accurate and extensive electronic calculations have been performed is the hydrogen-molecule ion,  $H_2^+$ . The Schrodinger equation for this system has been solved exactly (in the Born - Oppenheimer approximation) for several bound states (Bates, Ledsham and Stewart, 1953) and the transition energy and dipole matrix element have been calculated for a range of internuclear separations for several transitions (Madsen and Peek 1971, Ramaker and Peek 1973). In the present note, two  $H_2^+$  electronic transitions,  $1s\sigma_g \rightarrow 2p\sigma_u$  and  $1s\sigma_g \rightarrow 2p\pi_u$ , are studied which exemplify features of transitions between two-centre electronic wavefunctions. The transient  $H_2^+$  ions may be considered to form in binary collisions between H atoms and  $H^+$  ions in a (low temperature) hydrogen plasma. We shall not use the treatment of Bates (1952) to determine an absorption opacity, but in order to examine the physical processes occurring, we shall

consider the molecular oscillator strength  $f_{i \rightarrow f}$ . This is given (in atomic units) by

$$f_{i \rightarrow f} = \frac{2}{3} (\epsilon_f - \epsilon_i) g_{i \rightarrow f} |I_{i \rightarrow f}|^2$$

where  $\epsilon_f - \epsilon_i$  is the energy difference between initial and final states,  $g_{i \rightarrow f}$  is the degeneracy factor (Mulliken, 1939) and  $I_{i \rightarrow f}$  is the dipole matrix element for the transition

$$I_{i \rightarrow f} = \langle \psi_i(\underline{r}) | \underline{r} | \psi_f(\underline{r}) \rangle$$

with the initial and final electronic wavefunctions given by  $\psi_i(\underline{r})$  and  $\psi_f(\underline{r})$  respectively. The values of  $\epsilon_f - \epsilon_i$ ,  $|I_{i \rightarrow f}|^2$  and  $f_{i \rightarrow f}$  are tabulated for a range of internuclear separations in tables 1 and 2 and the oscillator strengths are plotted in figure 1 to show their dependence on internuclear separation.

For the  $1s\sigma_g \rightarrow 2p\sigma_u$  transition, as the nuclei separate the oscillator strength decreases to zero. This is because in the separated atom limit this corresponds to the atomic 'transition'  $1s \rightarrow 1s$ . The influence of the plasma is therefore to introduce an absorption mechanism not seen in the isolated atom and which could not have been predicted by first-order perturbation of the hydrogen atom by the neighbouring proton. It is necessary to consider the solution of the Schrodinger equation in a two-centre system to obtain such 'bonding' and 'antibonding' solutions. Transition of an electron between 'bonding' and 'antibonding' orbitals by absorption of a photon rearranges the electronic distribution between the nuclei. Because, in the limit of large internuclear separation the transition energy tends to zero, this results when the nuclei separate in the transfer of that energy to the kinetic motion of the ions. This coupling between radiation and ionic kinetic energy is evident only by the solution of the electronic wave equation in a two-centre system.

The molecular transition  $1s\sigma_g \rightarrow 2p\pi_u$  corresponds to the atomic

transitions  $1s \rightarrow 2p_{\pm 1}$  in both united and separated atom limits and the oscillator strength is in each case 0.278. The ratio

$$(f_{1s\sigma_g \rightarrow 2p\pi_u} - f_{1s \rightarrow 2p_{\pm 1}}) / f_{1s \rightarrow 2p_{\pm 1}}$$

is, therefore, a measure of the contribution to the oscillator strength from molecular effects and is tabulated in table 1. It can be seen to be significant even for large values of the internuclear separation. Although in the separated atom limit, the energy difference between  $1s\sigma_g$  and  $2p\pi_u$  is 0.375 a.u., there exist internuclear separations (table 1) for which the energy difference is less than this value. For photon absorption at such a separation in the transient molecule, the excitation energy as the nuclei separate is partly made up from the absorbed photon energy and partly from some fraction of the initial kinetic energy of the ions. If the photon energy is greater than the excitation energy as the nuclei separate, then the excess energy appears as ionic kinetic energy.

At high densities, the binary collision approximation fails. Treating the plasma by a similar technique to that described above would require multi-centre wavefunctions and in the limit of very high density where the plasma is thought to have an extended (solid-like) structure, the molecular orbitals will most easily be classified into electronic bands. The techniques of solid-state theory will at this point most readily apply.

### 3. Conclusions

In this note, the transient molecules formed by collisions between plasma species have been investigated for the case of a hydrogen plasma containing H atoms and  $H^+$  ions by using exact solutions of the Schrodinger equation for the  $H_2^+$  molecule. Three major differences with the usual treatment of the electronic structure have been found

- (i) The two-centre treatment predicts the existence of absorption processes not accounted for in a single-centre description.



(ii) The average oscillator strength of a transition that is allowed in the limit of large internuclear separation may be significantly altered in a two-centre description.

(iii) A coupling between radiation and ionic kinetic energy occurs which has not previously been described.

Although only electric-dipole photon absorption processes have been investigated in this report, the same considerations could be applied to electron-impact excitation and ionisation processes.

In discussing the ionic motion we have also assumed that the Born-Oppenheimer approximation holds and that the ions behave classically. In future work it is hoped to both provide more quantitative estimates of the effects predicted in this note and investigate the limitations of the assumptions made.



Table 1  $1s\sigma_g \rightarrow 2p\pi_u$   $H_2^+$  oscillator strengths

Internuclear separation $R^*$	$ I_{1s\sigma_g \rightarrow 2p\pi_u} ^{2*†}$	$\epsilon_{2p\pi_u}^{-\epsilon_{1s\sigma_g}}^{*†}$	$f_{1s\sigma_g \rightarrow 2p\pi_u}$	$\frac{f_{1s\sigma_g \rightarrow 2p\pi_u} - f_{1s \rightarrow 2p_{\pm 1}}}{f_{1s \rightarrow 2p_{\pm 1}}}$
$0^+$	0.139	1.500	0.278	0.0
1	0.302	0.978	0.393	0.42
2	0.512	0.674	0.460	0.66
3	0.684	0.524	0.479	0.73
4	0.784	0.445	0.466	0.68
5	0.800	0.403	0.430	0.55
6	0.755	0.382	0.384	0.38
7	0.685	0.372	0.339	0.22
8	0.619	0.368	0.304	0.09
9	0.568	0.367	0.278	0.0
10	0.534	0.368	0.262	-0.06
11	0.514	0.369	0.253	-0.09
12	0.505	0.370	0.249	-0.10
13	0.504	0.371	0.249	-0.10
14	0.508	0.372	0.252	-0.09
15	0.514	0.373	0.256	-0.08
16	0.521	0.374	0.260	-0.06
17	0.528	0.374	0.264	-0.05
18	0.534	0.375	0.267	-0.04
20	0.544	0.375	0.272	-0.02
25	0.553	0.375	0.277	0.0
30	0.555	0.375	0.277	0.0
$\infty^{++}$	0.555	0.375	0.278	0.0

\* In atomic units

+  $He^+$  transition  $1s \rightarrow 2p_{\pm 1}$

++ H transition  $1s \rightarrow 2p_{\pm 1}$

† Values taken from Madsen and Peek (1971) (except  $R = 0$  and  $\infty$ )

‡ Values taken from Ramaker and Peek(1973) (except  $R = 0$  and  $\infty$ )

Table 2  $1s\sigma_g \rightarrow 2p\sigma_u$   $\text{H}_2^+$  oscillator strengths

Internuclear separation $R^*$	$ I_{1s\sigma_g \rightarrow 2p\sigma_u} ^{2*†}$	$\epsilon_{2p\sigma_u} - \epsilon_{1s\sigma_g}^{*†}$	$f_{1s\sigma_g \rightarrow 2p\sigma_u}^{\ddagger}$
$0^+$	$1.39 \times 10^{-1}$	1.50	$1.39 \times 10^{-1}$
1	$4.55 \times 10^{-1}$	$8.87 \times 10^{-1}$	$2.69 \times 10^{-1}$
2	1.10	$4.35 \times 10^{-1}$	$3.20 \times 10^{-1}$
3	2.05	$2.09 \times 10^{-1}$	$2.87 \times 10^{-1}$
4	3.50	$1.01 \times 10^{-1}$	$2.35 \times 10^{-1}$
5	5.57	$4.71 \times 10^{-2}$	$1.75 \times 10^{-1}$
6	8.29	$2.13 \times 10^{-2}$	$1.18 \times 10^{-1}$
8	$1.54 \times 10^1$	$3.96 \times 10^{-2}$	$4.07 \times 10^{-2}$
10	$2.45 \times 10^1$	$6.78 \times 10^{-4}$	$1.11 \times 10^{-2}$
15	$5.60 \times 10^1$	$6.88 \times 10^{-6}$	$2.56 \times 10^{-4}$
20	$9.98 \times 10^1$	$6.17 \times 10^{-8}$	$4.10 \times 10^{-6}$
$\infty^{++}$	0.0	0.0	0.0

\* In atomic units

+  $\text{He}^+$  transition  $1s \rightarrow 2p_0$

++ H 'transition'  $1s \rightarrow 1s$

† Values taken from Madsen and Peek (1971) (except  $R = 0$  and  $\infty$ )

‡ Values taken from Ramaker and Peek (1973) (except  $R = 0$  and  $\infty$ )

§ Some of the oscillator strengths differ from the (less accurate) calculations of Bates (1951).

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FIGURE 1 THE DEPENDENCE OF OSCILLATOR STRENGTH  
ON INTERNUCLEAR SEPARATION  $1s\sigma_g \rightarrow 2p\pi_u$  AND  
 $1s\sigma_g \rightarrow 2p\sigma_u$  IN  $H_2^+$

