TWO-CENTRE ELECTRONIC WAVE FUNCTIONS IN PLASMAS

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Résumé

La structure électronique apparaissant lors de collisions entre ions dans un plasma est traitée en termes de fonctions d'onde à deux-centres. Les solutions exactes de l'équation de Schrödinger pour la molécule de H_2^+ sont utilisées pour décrire les collisions entre atomes H et ions H^+ dans un plasma d'hydrogène. Cette "chimie transitoire" montre l'existence de transitions qui ne sont pas prises en considération habituellement lors des traitements courants "uni-centre", et un couplage entre l'énergie de radiation et l'énergie cinétique ionique qui n'a pas été décrit auparavant.

Abstract

The electronic structure occuring during collisions between ions in a plasma is considered in terms of two-centre wave functions. 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

There are two general approaches to the calculation of bound electronic structure in a plasma. The first starts with an isolated ion, introducing the effect of the surrounding plasma by perturbarion theory. This is the principal method used in the calculation of line shapes. In the second

approach 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.

Several authors have considered the use of molecular wave functions to
describe the influence on bound electronic structure of the surrounding
ions in the plasma. Bates (1952) has investigated the contribution to the
radiative opacity of stellar atmospheres arising from absorption by H_2^+
ions

$$H_2^+ \ (1s\sigma_g) + h\nu \rightarrow H + H^+ \ (2p\sigma_u)$$
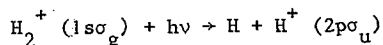
and from the transient molecule formed by colliding H atoms and H^+ ions

$$H + H^+ \ (1s\sigma_g) + h\nu \rightarrow H + H^+ \ (2p\sigma_u)$$
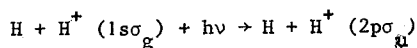
Bates' (1952)assumption of classical ion motion is relaxed in several
subsequent papers (Sando and Wormhoudt 1973, Szudy and Bayliss 1975, Le
Quang Rang and Voslamber 1975). The concept of transient molecule
formation in a plasma has also been applied to the calculation of line
shapes and in particular quasi-molecular satellites (eg Stewart, Peek and
Cooper 1973).

The purpose of the present work is 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
treatments. 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) we assume the validity of the Born-
Oppenhiemer 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 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 Schroedinger equation for

this system has been solved exactly (in the Born-Oppenhiemer approximation)

for several bound states (Bates, Ledsham and Stewart, 1953) and the

transition energies and dipole matrix-elements have been calculated for a

range of internuclear separations for several transitions (Madsen and Peek

1971, Ramaker and Peek 1973). In the present work, two representative H_2^+

electronic transitions, $1s\sigma_g \rightarrow 2p\sigma_u$ and $1s\sigma_g \rightarrow 2p\pi_u$, are studied. The

transient H_2^+ ions may be considered to form in binary collisions betwen 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 consider the

molecular oscillatior 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

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

Internuclear separation $R*$	$\lvert I_{1s\sigma_g \to 2p\pi_u}\rvert^{2*\ddagger}$	$\varepsilon_{2p\pi_u} - \varepsilon_{1s\sigma_g}$ *†	$f_{1s\sigma_g \to 2p\pi_u}$	$\dfrac{f_{1s\sigma_g \to 2p\pi_u} - f_{1s \to 2p_{\pm 1}}}{f_{1s \to 2p_{\pm 1}}}$
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	0.63
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
∞ ++	0.555	0.375	0.278	0.0

*   In atomic units

+ He^+ transitiion $1s \to 2p_{\pm 1}$

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

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

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

Table 2 $1s\sigma_g \to 2p\sigma_u$ H_2^+ oscillator strengths

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

* In atomic units

+ He$^+$ transition $1s \to 2p_0$

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

† Values taken from Madsen and Peek (1971) (except R = 0 and ∞)

‡ Values taken from Ramaker and Peek (1973)(except R = 0 and ∞)

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

necessary to consider the solution of the Schroedinger 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.
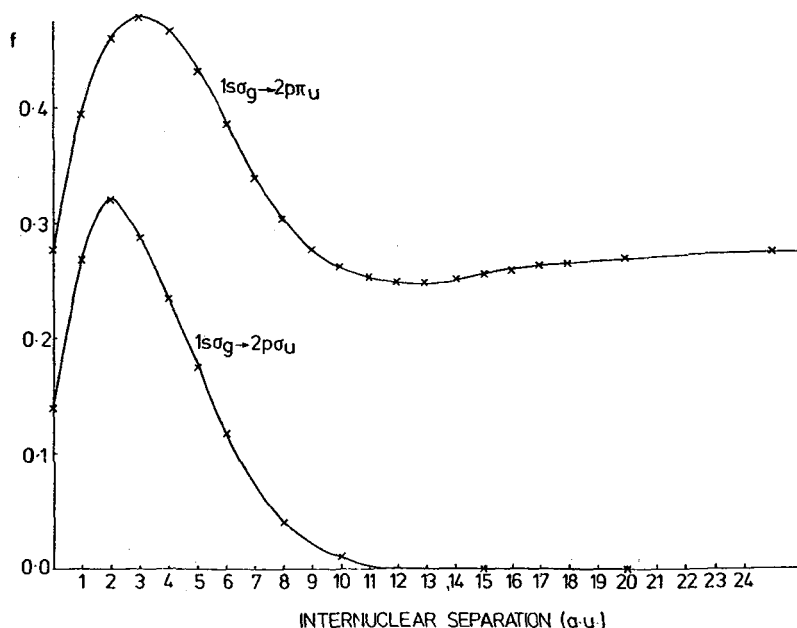
Figure 1. The dependence of oscillator strength on internuclear separation

for the transitions $1s\sigma_g \rightarrow 2p\sigma_u$ and $1s\sigma_g \rightarrow 2p\pi_u$ in H_2^+.

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. Conclusion

In this paper, 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 Schroedinger equation for the H_2^+ molecule. Three major differences from 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 in this work electric-dipole absorption has been investigated, the same considerations applied to electron-impact excitation processes predict the existence of a new coupling between electronic kinetic energy and ionic kinetic energy.

In future work it is hoped to both provide more quantitative estimates of the effects predicted   here   and investigate the limitations of the assumptions made.

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