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C.I. CALCULATIONS IN THE SILICON SEQUENCE

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Abstract - Large configuration interaction expansions are used to evaluate oscillator strengths of $3p^1-3p^0$, $3s^23p^2-3s3p^3$ and $-3s^33p^4s$; $3p^2-3p^0$, $3s^23p^2-3s3p^3$ and $-3s^33p^3d$ transitions in Si I, P II and S III. Values obtained in L-S coupling are satisfactory for all the transitions except those involving the $3p3d$ states where relativistic effects are expected to be important.

1. INTRODUCTION
There have been a number of recent experimental studies of transitions in members of the silicon iso-electronic sequence [1-7]. Corresponding theoretical studies have concentrated on transitions of the form $3s^23p^2-3s3p^3$. Aymar [8] used a parametric potential including spin-orbit interactions to investigate the $3p^2-3p^0$, $3p^0$ transitions for Si I through Ca VII. Even though the number of configurations was small, the same cancellation effects were evident as were found by Beck and Sinanoglu [9,10] with their more elaborate NCMET prescription. The cancellation is due to major configuration interaction (C.I.) between $3s3p^3$ and $3s^23p^3d$ (and $3s^33p^4s$ for $3p^0$, though to a lesser extent). Hussbaumer [11], in a study of the iso-electronic Fe XIII, has pointed out the dangers of limited C.I. in such situations. For example, the inclusion of the configuration $3s3p^3d^2$ results in a substantial change (even of sign) in the expansion coefficients of the dominant configurations, even though its own coefficient is an order of magnitude smaller. The purpose of this paper is to extend the NCMET calculation by the inclusion of all-external correlation, within an L-S framework, and to present theoretical values for transitions previously considered only by experimental techniques.

2. WAVE FUNCTIONS AND ENERGY LEVELS
Because of the anticipated C.I. between the low-lying excited state levels, we considered it necessary to obtain as good a representation as possible of these as well as of the ground state. The type of calculation is similar to that employed earlier [12,13] in which the radial functions $P_nk$ are analytic finite sums of Slater-type orbitals. The $1s,2s,2p,3s,3p$ functions were chosen as the HF functions of the ground $3p^e$ state [14], while the remaining functions contain precisely $(n-2)$ basis functions so that the orthonormality integrals determine the basis coefficients in each case. This essentially leaves the exponents of the Slater functions as parameters which may be varied.

The 3d function was varied to optimize the important $3s\rightarrow 3d$ correlation in the ground state. The $3s^23p^3d$ state was then represented by a combination of $3s^23p^3d$ and $3s^23p^4d$, with the 4d exponents being optimized on the correct eigenvalue in a CI expansion, including where appropriate $3s3p^3$ and $3s^23p^4s$. The 4s function was optimized on the eigenvalue dominated by the configuration $3s^33p^4s$. The $n$-values of our radial functions therefore do not necessarily have spectroscopic significance.

In addition, we determined a 5d function to account for the semi-internal effect $3s3p^3 + 3s^3p^4n$, while the 4f function was determined by optimizing $3s3p^3 + 3s3p^24f$. Just as the correla-
tion 3d of the ground state is different from the excited state's spectroscopic 3d (represented in our calculations by a combination of our 3d and 4d functions), so the 3p functions of the states are not identical. We determined the 4p function as a correction to the 3p for the excited states. Finally, we determined 5s and 5p functions to optimize the M-shell correlation of the ground state. We found little difference between the sets of radial functions for the 3p0 and 3p0 states, and for the final calculations we used the same set of functions for all states.

The energy splittings between the ground state and the 3s2 3p2 3p0, 3p0, and 3s2 3p4s 3p0 states were in generally good agreement with experimental splittings as may be seen from Table I. The 3s2 3p3d states were consistently higher than experiment, by several thousand cm⁻¹, although the order of the multiplets arising from the configuration was correct. It is not clear to us why this should be. Relativistic effects are likely to be important here (see later) although the fine structure splitting of the states involved is at most a few hundred cm⁻¹. It is possible that an important configuration has been omitted (though we have been careful to check these) or that further refinements in the radial functions are needed. For Si I and P II, the different states are well separated. However, for S III, the 3p4s 3p0 and 3p3d 3p0 states lie close together, and the error in the latter results in our calculation placing them in the wrong order. The interaction between them, which is substantial, could well be wrong.

3. OSCILLATOR STRENGTHS

One of the motivations of this work was the f-value obtained by Livingston et al. [1] for the 3s2 3p2 3p - 3s3p3 3p transition in P II. The lifetime is twice as long as that obtained previously [2,15]. The earlier values had been confined by NCMET calculations [9]; we wished to see if all-external correlation had the effect of reducing the f-value. The result shown in Table I represents correlation only within the M-shell, but the value is below that of NCMET, and is, in fact, in very good agreement with the relatively simple calculation of Aymar [8]. That this is true also for S III suggests that her values for more highly ionized systems are also reliable. It

<table>
<thead>
<tr>
<th>Table I</th>
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<tbody>
<tr>
<td><strong>Absorption oscillator strengths (L-S coupling)</strong></td>
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<tr>
<td>3s2 3p2 3p - 3s3p3 3p</td>
</tr>
<tr>
<td>P II</td>
</tr>
<tr>
<td>f_f</td>
</tr>
<tr>
<td>f_v</td>
</tr>
<tr>
<td>ΔE(th.) (in a.u.)</td>
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<tr>
<td>ΔE(exp.)</td>
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<tr>
<td>f_exp</td>
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<tr>
<td></td>
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<tr>
<td>f_th. (length)</td>
</tr>
<tr>
<td>3s2 3p2 3p - 3s2 3p4s 3p</td>
</tr>
<tr>
<td>Si I</td>
</tr>
<tr>
<td>f_f</td>
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<tr>
<td>f_v</td>
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<td>ΔE(exp.)</td>
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<tr>
<td>f_exp</td>
</tr>
<tr>
<td>3s2 3p2 3p - 3s3p3 3d</td>
</tr>
<tr>
<td>P II</td>
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<td>f_f</td>
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<td>ΔE(exp.)</td>
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<td>f_exp</td>
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</table>

^a Livingston et al. [1]  
^b Curtis et al. [2]  
^c Savage and Lawrence [15]  
^d Aymar [8]  
^e Beck and Sinanoglu [9]  
^f Livingston et al. [3]  
^g Sinanoglu and Beck [10]  
^h Dumont et al. [7]
is, however, difficult to place any reliance on
more than the first significant figure for such
transitions. We performed a calculation which was
essentially NCMET in style but including 4s in the
HF sea. The length and velocity values for P II
were 0.017 and 0.021 for the lowest transition,
while the values for the transition involving
3s^2 3p^4 s were hardly changed. The cause of the
change was a modification in the weightings of
the configurations dominating the upper state and the
cancellation.

Serious cancellations do not occur in
the 3p^2 - 3p^4 s transition for Si I and P II, and
agreement with experiment is very good. For
Si I, work by Garz [3] suggests an experimental
value up to 10% higher than that of Savage and
Lawrence [15], although the lifetime of the
upper levels varies somewhat with J. Even though
we have doubts about our calculation for S III,
because of the possible incorrect interaction
between 3p^4 s and 3p^4 d, our f-value is in agreement
with recent experiment [7].

The 3P - 3D transitions were not
pursued much beyond the NCMET level. Our
calculation of 3s^23p^2 - 3s3p^3 confirms the earlier
result of Sinanoglu and Beck [10]. The 3p^2 - 3p^3
oscillator strength appears in fairly good
agreement with the experimental work of Livingston
et al. [1].

4. RELATIVISTIC EFFECTS

Our main purpose has been to
calculate multiplet oscillator strengths. But for
medium sized atoms, it is important to look at how
relativistic effects (spin-orbit interactions etc.)
change such results. We have made some prelimi-
ary investigations in this direction for P II.
We find very little multiplet interactions for the
same J in the 3s3p^3 states (though this situation
does not obtain for higher members of the sequence
[11]). There is only a small interaction between
the 3p^4 s 3P_1 and 1P_1 states, and in view of the
lack of large cancellation effects in transitions
involving this 3P state we do not feel the
inclusion of relativistic effects would be
important. Accordingly, for the first three
transitions displayed in Table I, we believe that
L-S coupling gives a satisfactory representation of
the states involved, except possibly for 3p^2 -
3p^4 s in S III.

Major C.I. arises in the 3p3d states due
to relativistic effects. In initial, rather
simple calculations, we have not found any
improvement in the positions of the 3p3d states as
a result of relativistic effects. The major
theoretical difficulty is that of representing
accurately the small splitting between the 3p3d,
3P and 3D levels, which is required for the
correct interaction between them. More details
will be given in a later publication.

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