Systematic studies of highly excited Rydberg states in ions with two valance electrons

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Abstract
A method, based on the multiconfiguration Hartree–Fock approach, for ab initio calculations of Rydberg states has been developed. The method has been tested for a number of highly excited Rydberg states, with quantum numbers \( l = 4–8 \) and \( n \leq 9 \), in Mg-like and Be-like ions. The results are compared with Hartree–Fock calculations to investigate the influence of correlation and, to a lesser extent, relativistic effects. The theoretical spectra for Cl VI and the lifetimes of the 2s6g-levels in O V are in excellent agreement with experimental results. More limited calculations have also been done for some Rydberg series in S V and Ar VII to illustrate the changing influence of perturbers along the isoelectronic sequence. The difficulties of using isoelectronic extrapolation/interpolation in making predictions for this kind of systems are discussed.

1. Introduction

Much work has been done on magnesium-like systems. Experimental measurements of a large number of energy levels are available, for example, Mg I and Al II (Sansonetti and Martin 2005), P IV (Zetterberg and Magnusson 1977) and S V (Joelsson et al 1981). The lifetimes for some levels in Mg-like ions have also been measured with beam–foil spectroscopy, for example, in Cl VI (Engström et al 1995, Berry et al 1976) and Ar VII (Berry et al 1976). Many ab initio calculations using a wide range of different methods have also been done for calculating transition rates and lifetimes. To mention just a few, lifetimes in P IV, S V and Cl VI have been calculated using CIV3 (Brage and Hibbert 1989), Si III, S V and Fe XV using CIV3 and RQDO (Almaraz et al 2000), Mg I–Ti XII using MCRRPA (Chou et al 1993), Al II–S V using MCDHF (Zou and Froese Fischer 2000, 2001) and Mg I–Zn XIX using MCHF (Tachiev and Froese Fischer 2002). Furthermore, Biemont et al (2002) made calculations using
HFR + CP and a semi-empirical fitting procedure for transitions in K VII and Steiner and Curtis (2004) made calculations on S V and Fe XV testing a semi-empirical method which could be used to calculate branching fractions and, together with known transition rates, to predict the rate of other transitions. Even though there is a lot of work done for these types of systems, there is very little concerning Rydberg states. Among the works mentioned above, only Zetterberg and Magnusson (1977), Joelsson et al (1981) and Almaraz et al (2000) include a treatment of these types of states. Especially, in the latter the transition probability for transitions of the type 3s^2 1S–3sp^1 1P with n ≤ 8 has been calculated.

The aim of our work was to develop a straightforward method for ab initio calculations of the Rydberg states, which could be used to simplify the analysis of an experimental spectrum. The initial interest for calculating such structures came from a desire to understand spectra resulting from the passage of highly charged ions through micro-capillary targets (see, for example, Morishita et al (2004)). In these experiments, highly charged ions (typically Ar^{7+}) capture one or more electrons in their interaction with the capillary surface producing ions in highly excited states. The spectra observed in these experiments were interpreted by comparisons with MCHF calculations (Morishita et al 2004). However, the problem of calculating high n, l transitions in Mg-like ions was deemed interesting enough for a more comprehensive study. To test our method, this study focuses on Mg-like chlorine to compare with Bashkin et al (1973) and high-resolution spectra obtained at the Lund beam–foil spectroscopy facility. To show the difficulties of using isoelectronic extrapolation/interpolation in making predictions for this kind of systems, calculations have also been done on S V and Ar VII. As a further test of the method, the lifetime of some levels in O V has been calculated and compared to experimental values (Kink et al 1999).

A Rydberg series is usually defined as all levels that can be formed by a single excitation from the ground configuration, with common values for all angular momenta and only differing in the n-quantum number of the outermost electron. In magnesium-like ions, where the ground configuration is 1s^2 2s^2 2p^6 3s^2, a Rydberg series can therefore be represented as

\[ 1s^2 2s^2 2p^6 3s^2 l 3^2 S \]

\[ n > 3. \]

In this paper we develop a theoretical method to treat a whole Rydberg series within one calculation. This is a non-trivial task due to, among other things, the presence of fairly low-lying doubly excited states, so-called perturbers or members of displaced systems, of the form

\[ 1s^2 2s^2 2p^6 3s^2 l 3^2 S \]

\[ n > 3. \]

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\[ 1s^2 2s^2 2p^6 3s^2 l 3^2 S \]

\[ n > 3. \]

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Two examples of such perturbers are 1s^2 2s^2 2p^6 3p^4 1G and 1s^2 2s^2 2p^6 3d^2 1G which can perturb the 3s^2 1G Rydberg series. When comparing Hartree–Fock results with more extensive calculations, it is clear that a very irregular structure can be observed for many Rydberg states.

2. Theoretical methods

The atoms studied in this paper are the three Mg-like ions S^{4+}, Cl^{5+} and Ar^{6+} and the Be-like ion O^{6+}. Since these atoms are fairly light a fully relativistic treatment is not necessary. We have therefore based our approach on the Breit–Pauli Hamiltonian, which consists of three parts

\[ H_{BP} = H_{NR} + H_{RS} + H_{FS}. \]
In this, $H_{\text{NR}}$ is the non-relativistic Hamiltonian

$$H = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_i - \frac{Z}{r_i} \right) + \sum_{i<j}^{N} \frac{1}{r_{ij}}.$$ 

$H_{\text{RS}}$ consists of the relativistic shift operators and $H_{\text{FS}}$ the fine-structure operators (Glass and Hibbert 1978).

The computations are performed using the multiconfiguration Hartree–Fock (MCHF) package of Froese Fischer et al. (1997). In this method, the calculations are divided into two parts. The first is the variational determination of the radial part of the spin–orbitals

$$\phi(q) = \frac{1}{r} P_{nlm}(r) Y_{lml}(\theta, \phi) \chi(\sigma).$$

The variational method is defined by the non-relativistic Hamiltonian, $H_{\text{NR}}$ and as a trial function we use an expansion of configuration state functions (CSFs), $\Phi(\gamma_iLS)$

$$\Psi(\gamma J) = \sum_{i=1}^{N} c_i \Phi(\gamma_i L_i S_i J).$$

where $\gamma_i$ represents all quantum numbers other than $L$ and $S$ required to uniquely define a coupled, antisymmetric, linear combination of one electron spin–orbitals.

In the second part of the method, the relativistic effects and the fine structure are added in a configuration interaction (CI) approach. Since the fine-structure part of the Breit–Pauli Hamiltonian commutes only with the total angular momentum $J$ and not with the separate $L$ and $S$ operators, the eigenfunctions to this Hamiltonian are represented as eigenfunctions of $J^2$ and $J_z$. This implies that the linear combination describing the wavefunction in the multiconfiguration approximation is given by

$$\Psi(\gamma J) = \sum_{i=1}^{N} c_i \Phi(\gamma_i L_i S_i J).$$

### 2.1. The layered method

The aim of this paper is to design a computational method that treats a number of Rydberg states simultaneously. For this we derived a method called the *layered method*. We describe the method for a Mg-like ion, but it can be used in a similar way for any other two-electron system. In this method, we define three different sets of CSFs for each Rydberg series (see table 1). First, the spectroscopic set which contains the Rydberg states we are interested in, second, the set of perturbers, which are states that are embedded in the part of the Rydberg series we are investigating, and third, the correlation CSFs, which are included to improve the representation of correlation. As can be seen in the table, we limit our approach to only take into account valence correlation, that is, we keep the 1s$^2$2s$^2$2p$^6$ core fixed and closed throughout the calculations.

To describe our calculations in more detail we will use the 3snh Rydberg series as an example (see the second row of table 1). We start by making a frozen-core Hartree–Fock calculation for the spectroscopic CSFs. The corresponding orbitals are then kept fixed for the rest of the calculations. In our example, this corresponds to the four members of the 3snh Rydberg series, where $n = 6–9$.

Next, we look for possible perturbers. These can be detected by Hartree–Fock calculations, where we compare the energies of potential perturbers with those of the spectroscopic states. When these are sufficiently similar, the perturbers are included but the corresponding Hartree–Fock radial functions are kept unchanged. In our example, there is one such perturber, 3p5g, situated somewhere between the four members of the 3snh series.
Table 1. The configurations included in the shape layered method calculations for different Rydberg series. Both the singlet and the triplet states of the given symmetry are included, unless otherwise stated.

<table>
<thead>
<tr>
<th>Series</th>
<th>Spectroscopic</th>
<th>Perturbers</th>
<th>Correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td>3sng</td>
<td>3s(5–9)g</td>
<td>3p(4–5)g, 3d1 G</td>
<td>3s(10)g, 4s(5–10)g, 3p6f, 4p(4–6)f, 3p6h, 4p6h, 3d4d, 3d(5–10)g, 3d7i</td>
</tr>
<tr>
<td>3sh</td>
<td>3s(6–9)h</td>
<td>3p5g</td>
<td>3s10h, 4s(6–10)h, 3p6g, 4p5–6g, 3p7i, 4p7i, 3d6–10h, 3d4f, 3d8k</td>
</tr>
<tr>
<td>3snl</td>
<td>3s(7–9)il</td>
<td>3s10i, 4s(7–10)i, 3p6h, 3p8k, 3d5g, 3d7–10i, 3d9l</td>
<td></td>
</tr>
<tr>
<td>3sni</td>
<td>3s(8–9)ik</td>
<td>3s10k, 4s(8–10)k, 3p7i, 3p9f, 3d6h, 3d8–10k, 3d10m</td>
<td></td>
</tr>
<tr>
<td>3skl</td>
<td>3s(9–10)l</td>
<td>3s10l, 4s(9–10)l, 3p8k, 3p10m, 3d7i, 3d(9–10)l, 3d11n</td>
<td></td>
</tr>
</tbody>
</table>

The next step is to add a configuration for each of the other possible symmetries that are part of the first and second displaced systems, i.e., in our case configurations of the form 3pnl and 3dnl. These are optimized on the main states (Rydberg series and perturbers) and will therefore belong to the correlation set of CSFs. In our calculations, these are 3p7i, 3d4f and 3d6h.

It is a limitation that the orbitals in the spectroscopic and perturber CSFs are not reoptimized after the correlation CSFs are added. To compensate for this we include a number of states that can be formed from the existing orbitals and one new orbital for each l symmetry. In our example, this is represented by adjusting the 3snh series, including 3s10h and 4s9h (n = 5–10) and optimizing 4s and 10h. The same strategy for the perturbers leads us to include 3p6g, 4p5g and 4p6g.

When all new configurations are added this final MCHF optimization represents a whole Rydberg series in one single calculation. For two orbitals with large values of n and l (the 8k orbital in the 3sni calculation and the 11n orbital in the 3sni calculation), we ran into convergence problems and used the screened hydrogenic approximation instead.

2.2. Extended layered method

The method outlined above do not allow for the fact that relativistic effects can cause mixing between members of different Rydberg series since the LS-approximation is not valid due to the close proximity of a different l state for the same n and at the same time the fine structure could be large due to the open 3p-shell in the perturber. We have, therefore, also developed a different method, the extended layered method, where we include all states of the same parity and J, but belonging to different Rydberg series and values of L and S. To account for the reduced flexibility in the orbital sets, we add some extra configurations, as given in table 2.

In practice, the calculations are performed in a stepwise procedure, just as in the layered approach. Again, for some of the high n and l states we encounter convergence problems and are therefore forced to include some orbitals as screened hydrogenic. These are 8k, 10m and 11n in the calculations of the even states and 7i, 9l and 10m for the odd states.

2.3. Fully variational method

The methods described so far have not used the full potential of the MCHF method in the sense that we only optimize one set of orbitals at a time instead of varying all in a fully variational
Table 2. The configurations included in the extended layered method for even and odd Rydberg series. Each configuration represents both the singlet and triplet terms, unless otherwise stated.

<table>
<thead>
<tr>
<th>Parity</th>
<th>Spectroscopic</th>
<th>Perturbers</th>
<th>Correlations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Even</td>
<td>3s(5–9)g, 3s7–9i I, 3s9/2 L</td>
<td>3p(4–5)f G, 3d2 3/2 G</td>
<td>3s10g G, 4s(5–10)g G, 3p6f G, 4p(4–6)f G, 3p6h G, 4p6h G, 3d4d G, 3d(5–10)g G, 3d(7–10)i G, 4d10i G, 3s10 L, 4s(7–10)i I, 3p6h I, 4p6h I, 3p8k I, 4p8k I, 3d(5–10)g I, 4d10g I, 3d(7–10)i I, 4d10i L, 3d(9–10)l L, 4d10f I, 3s10f L, 4s(9–10)f L, 3p8k L, 3p10m L, 4p10m L, 3d(7–10)i L, 4d10i L, 3d(9–10)i L, 4d10f L, 3d11n L, 4d11n L</td>
</tr>
<tr>
<td>Odd</td>
<td>3s(6–9)h, 3s8–9k</td>
<td>3p5g H</td>
<td>3s10h H, 4s(6–10)h H, 3p6g H, 4p(5–6)g H, 3p7i H, 4p7i H, 3d4f H, 3d(6–10)h H, 3d(8–10)k H, 3s10k K, 4s(8–10)k K, 3p7i K, 4p7i K, 3p9l K, 4p9l K, 3d(6–10)h K, 3d(8–10)l K, 3d10m K</td>
</tr>
</tbody>
</table>

Table 3. The configurations used in the fully variational method calculation for the 3sng 3/2 G Rydberg series. All states in the table are 3/2 G.

<table>
<thead>
<tr>
<th>Step</th>
<th>Added configurations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopic</td>
<td>3s5g, 3s6g, 3s7g, 3s8g, 3s9g</td>
</tr>
<tr>
<td>Perturbers</td>
<td>3p4f, 3p5f, 3d2</td>
</tr>
<tr>
<td>Shell 5</td>
<td>3d4d, 3d5d, 3d5g, 3f5f</td>
</tr>
<tr>
<td>Shell 6</td>
<td>3p6f, 3p6h, 3d6d, 3d6f, 4p6f, 3d6g, 4d6g, 4f6h, 5g6g</td>
</tr>
<tr>
<td>Shell 7</td>
<td>3p7f, 3d7f, 3d7g, 3p7h, 5d7g, 6f7f, 5f, 6h7h</td>
</tr>
<tr>
<td>Shell 8</td>
<td>3p8f, 3p8h, 3d8d, 3d8g, 4s8g, 4p8h, 4p8l, 7d8d, 6d8g, 6f8h, 7g8g</td>
</tr>
<tr>
<td>Shell 9</td>
<td>5s9g, 7p9f, 5p9h, 7d9g, 8f9f, 8h9f, 3p9f, 3p9h, 3d9d, 3d9g</td>
</tr>
<tr>
<td>Shell 10</td>
<td>6s10g, 8p10f, 6p10h, 9d10d, 8d10g, 8f10h, 9g10g</td>
</tr>
<tr>
<td>Shell i</td>
<td>3d7i, 5g7i, 3d8i, 4d8i, 4d8i, 6g8i, 7i8i, 5d9i, 7g9i, 3d9i, 6d10i, 8g10i, 9i10k</td>
</tr>
<tr>
<td>Shell k</td>
<td>4f9k, 6h9k, 5f9k, 7h9k, 8k9k, 6f10k, 8h10k</td>
</tr>
<tr>
<td>Shell l</td>
<td>5g9l, 7l9l, 6q10l, 8l10l, 9l10l</td>
</tr>
<tr>
<td>Shell m</td>
<td>6h10m, 8k10m</td>
</tr>
</tbody>
</table>

To estimate the limitations involved in this approach, we performed a third set of calculations for the 3sng 3/2 G Rydberg case. The expansions we used in this case are given in table 3. In this fully variational method, we start by making an HF calculation for the states of interest. Then we add perturbers and all other configurations with the same L up to a certain shell (see table 3). For each shell, we make an MCHF calculation where we only vary the new orbitals followed by an MCHF calculation where we let all the orbitals vary. We do encounter a few convergence problems (if we just add the configurations shell by shell), after and including shell 7. Hence, from shell 7 we only include configurations with orbitals with \( l \leq 5 \) and continue with this until shell 10. After that we include configurations with \( l = 6 \), then with
In the last two steps we can only let the new orbitals vary, but this will most certainly not affect the accuracy significantly due to the high \( n \) and \( l \) values.

### 2.4. O V calculations

As a separate test of the layered method, the lifetimes of the heavily perturbed 2s\(6g \, ^1\Sigma^+ \), \( ^3\Sigma \) levels in the Be-like ion O V are calculated for comparing with experimental values (Kink et al 1999). In principle, we make these calculations in the same manner as above, except that we optimize both the upper and lower configurations in the same calculations to assure orthogonality between all orbitals in the transition calculation. We perform eight calculations, four for the transitions 2s(4–5)f \( ^1\Sigma^+ \), \( ^3\Sigma \), and four for the transition 2p3d \( ^1\Sigma^+ \), \( ^3\Sigma \). In each calculation, we start by making HF calculations for the most important configurations in the way described above. When we include the correlation configurations, we start by optimizing the orbitals 7g and 6h on 2s\(6g \), then 6f and 3d on 2s(4–5)f (4d and 5f on 2p3d) and finally 3s and 3p on 2s\(6g \) and 2s(4–5)f (2s\(6g \) and 2p3d). We repeat this procedure until the orbitals have converged. Finally, we make a Breit–Pauli configuration interaction calculation and compute the transition rates.

### 3. Beam–foil experiments

Beams of chlorine ions at 1.5, 3.5 and 7 MeV were provided by the 3 MV Pelletron tandem accelerator in Lund. After acceleration and momentum analysis, the ion beam was further stripped and excited by a 5 \( \mu \)g cm\(^{-2} \) carbon foil in the beam–foil target chamber. Further details on the target chamber can be found in Engström and Håkansson (1991). Photons emitted by the decay of the foil-excited ions were dispersed by a 1 m Minuteman normal incidence spectrometer (310 NIV) equipped with a 600 lines mm\(^{-1} \) grating. Finally, the photons were detected using a Photometrics CH270 CCD camera employing a thin, back-illuminated EEV 15-11B chip (1024 \( \times \) 256 pixels). The chip was coated with Metachrome II to improve its response to UV light and cooled to \(-120^\circ\)C to reduce thermal noise. Additional details of the experimental arrangement, including discussions of the data collection mode, elimination of features caused by cosmic rays, etc can be found in Kink et al (1999).

Chlorine spectra were recorded between 3000 and 8000 Å. The grating was stepped 200 Å at a time and at each setting a 400 Å region was recorded on the CCD. Spectra were recorded both with and without optical filters to distinguish between lines in different spectral orders. Based on known charge state distributions for chlorine ions passing through 5 \( \mu \)g cm\(^{-2} \) carbon foils, the beam at 3.5 MeV is expected to maximize the production of Mg-like Cl, which is the spectrum under consideration in the current work. The spectra were wavelength calibrated using the known characteristics of the 1 m Minuteman normal incidence spectrometer, which is accurate enough for the present work.

### 4. Results and discussion

In table 4 we compare the three computational approaches. It is clear that the fully variational method should be considered the most accurate, but it does involve substantial convergence problems. We can see from table 4 that the two layered methods capture the same effects as the fully variational and that the deviations from HF for the two methods are very similar. If we compare the layered method and the extended layered method, there is no obvious difference in accuracy.
Systematic studies of highly excited Rydberg states

4.1. CI V

4.1.1. Effects of perturbers on the spectrum. In figure 1 we compare spectra from the extended layered method with spectra based on the HF method. To understand some of the changes in the spectra, we will use the plunging diagram in figure 3, which we will come back to in section 4.2. We first look at the \( n = 6–7 \) transitions. In the HF-spectrum there are only three closely separated peaks, where the first contains the \( 3s6g \) \( ^3G \)–\( 3s7h \) \( ^1H \), \( ^3H \) transitions, the second \( 3s6h \) \( ^1G \)–\( 3s7i \) \( ^1G \) and the third \( 3s6g \) \( ^1G \)–\( 3s7h \) \( ^1H \). In the correlated spectrum, on the other hand, we can see large differences in the structure. There is a small change for the first peak, belonging to the \( 3s6h \) \( ^1H \)–\( 3s7i \) \( ^1I \) transitions due to the \( 3s6h \) levels pressed down in energy by the the \( 3p5g \) perturber. The great changes of the spectrum are from the transitions to \( 3s6g \). The transitions \( 3s6g \) \( ^3G \)–\( 3s7h \) \( ^1H \) are changed by about 150 Å and \( 3s6g \) \( ^1G \)–\( 3s7h \) \( ^1H \) by no less than 560 Å . In figure 3 it is seen that the \( 3p4f \) perturber is just below \( 3s6g \) in energy in CI VI, resulting in a large perturbation. The reason for the uneven perturbation of \( 3s6g \) \( ^1G \) and \( ^3G \) is the \( 3d^2 \) \( ^1G \) perturber, not so much because of the direct interaction with \( 3s6g \) \( ^1G \), but rather due to the fact that this state is pressing \( 3p4f \) \( ^1G \) closer to \( 3s6g \) \( ^1G \) increasing the interaction between these two states.

<table>
<thead>
<tr>
<th>State</th>
<th>HF-layered</th>
<th>HF-extended layered</th>
<th>HF-fully variational</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 3s6g ) ( ^3G )</td>
<td>2440.34</td>
<td>2453.73</td>
<td>2483.80</td>
</tr>
<tr>
<td>( 3s6g ) ( ^3G )</td>
<td>-959.98</td>
<td>-956.03</td>
<td>-931.23</td>
</tr>
<tr>
<td>( 3s7g ) ( ^3G )</td>
<td>-50.26</td>
<td>-51.36</td>
<td>-55.09</td>
</tr>
<tr>
<td>( 3s8g ) ( ^3G )</td>
<td>-123.13</td>
<td>-122.47</td>
<td>-139.81</td>
</tr>
<tr>
<td>( 3s9g ) ( ^3G )</td>
<td>268.42</td>
<td>267.98</td>
<td>280.27</td>
</tr>
</tbody>
</table>

Figure 1. Spectra for CI VI.
Figure 2. Theoretical 3s7l–3s8l transitions in Cl VI (dashed) compared to an experimental spectrum recorded by the beam–foil technique (solid).

Looking at the spectra for the \( n = 7–8 \) and the \( n = 8–9 \) transitions, we see that transitions which do not involve any of the 3sng or 3snh levels are more or less unchanged going from HF to the correlated spectra. For the 3snh–3s\((n + 1)i\) transitions, the difference between the HF and the extended layered method increases with \( n \) because the 3snh Rydberg states get closer to the perturer 3p5g and the perturbation increases. For the 3s6h–3s7i transitions, the difference is about 30 Å whereas for 3s7h–3s8i it is 45 Å and 120 Å for 3s8h–3s9i. The differences between the two methods for the 3sng–3s\((n + 1)h\) transitions depend on both the perturbation of 3sng from above by 3p5g and the perturbation of 3sng from below by 3p4f and 3d². As mentioned above, the 3d²1G perturber is responsible for the large splitting between the transitions to 1G and 3G. This splitting differs by 400 Å between the two methods in the \( n = 6–7 \) spectrum, but decreases to only 60 Å in the \( n = 7–8 \) spectrum and in the \( n = 8–9 \) spectrum the effect has disappeared. If we follow the 3sng \( 1G–3s(n + 1)h \) transitions the two methods differ by 150 Å in the \( n = 6–7 \) spectrum and by 70 Å in both the \( n = 7–8 \) and \( 8–9 \) spectra. The reason that we get the same difference for the last two is a coincidence. The perturbation from below of 3s8g is smaller than 3s7g, but at the same time the perturbation from above of 3s9h is larger than 3s8h.

4.1.2. Comparisons with experiment. Figure 2 shows the good agreement between our theoretical results for the \( n = 7–8 \) transitions and the beam–foil spectrum. The figure gives the correct relative theoretical intensities whereas the absolute values have been adjusted to the experimental scale. The first peak is the transition between the perturbed configurations 3s7h and 3s8i, the second between 3s7i and 3s8k, the third and fourth between the two perturbed 3s7g and 3s8h where the first of these are the transitions to 1G and the second to 3G.

In table 5 we compare our calculated wavelengths with the experimental results of Bashkin et al (1973). For six of the eight lines, including the transition between the two perturbed configurations 3s5g and 3s7h, the agreement is good. The transition 3s7i–3s8k differs by
Table 5. A comparison between experimental and theoretical wavelengths of a few transitions in Cl VI.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\lambda_{\text{exp}}$ (Å)$^a$</th>
<th>$\lambda_{\text{this work}}$ (Å)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5g–7h</td>
<td>1256.0</td>
<td>1255.0–1259.1</td>
</tr>
<tr>
<td>5g–6h</td>
<td>1985.0</td>
<td>1981.5–1990.6</td>
</tr>
<tr>
<td>6h–8i</td>
<td>2071.0</td>
<td>2071.3–2071.4</td>
</tr>
<tr>
<td>7i–9k</td>
<td>3136.1</td>
<td>3137.4–3137.5</td>
</tr>
<tr>
<td>6g–7h</td>
<td>3271.0</td>
<td>3572.0–3582.2$^c$, 3993.4–3994.2$^d$</td>
</tr>
<tr>
<td>6h–7i</td>
<td>3407.5</td>
<td>3405.2–3405.7</td>
</tr>
<tr>
<td>7h–8i</td>
<td>5237.5</td>
<td>5236.5–5237.9</td>
</tr>
<tr>
<td>7i–8k</td>
<td>5277.5</td>
<td>5288.6–5288.9</td>
</tr>
</tbody>
</table>


$^b$ We give the shortest and longest wavelengths of the different transitions.

$^c$ Transitions to 3s6g $^3$G.

$^d$ Transitions to 3s6g $^1$G.

about 10 Å, significantly worse than the others, but this could be related to the convergence problems for orbitals with high $l$ described above. Finally, in the 3s6g–3s7h transition there are very large differences in wavelength if the lower level is $^1$G or $^3$G, and we give two separate values in our table. None of these fits with the experimental value, the closest are 300 Å larger. This is not surprising since Bashkin et al (1973) used isoelectronic interpolation as a method to assign the lines, without taking the severe perturbation into account and we question their designation for this line. It should be pointed out that the authors did mention that there could be a problem with perturbers for these transition, and we think there were.

4.2. Comparisons along the Mg-like isoelectronic sequence

As discussed above, the perturbers can have a very big impact on the spectrum for an ion (Joelsson et al 1981, Zetterberg and Magnusson 1977, Trigueiros et al 2001). Which perturbers are important and how will they perturb the spectra for different ions along an isoelectronic sequence can be studied by making a 'plunging diagram' (Froese Fischer 1978). All perturbers belong to doubly excited states and in most cases they will have an energy above the ionization limit in the neutral end of the sequence. As we move along the isoelectronic sequence, the perturbers will plunge through the 'normal' Rydberg series, that is, singly excited levels and perturb any state that happens to be close in energy. A plunging diagram for the most important perturbers along a part of the Mg-like isoelectronic sequence is presented in figure 3.

Referring to this diagram, large perturbations can be predicted for the 3sng Rydberg series along the isoelectronic sequence in S$^+$, Cl$^+$ and Ar$^{8+}$. Therefore, we have made some calculations for S$^{4+}$ and Ar$^{6+}$ to illustrate this effect.

In figure 4 we have made two plots which show the difference in wavelength between the HF and extended layered method along the isoelectronic sequence for the transitions $3s5g$ $^1$G–3s6h $^1$H, $3s7g$ $^1$G–3s8h $^1$H and $3s8g$ $^1$G–3s9h $^1$H. It is clear that the plunging configurations severely affect the structure.

We start by looking at the 3s8g–3s9h transitions. In S$^+$ both the transitions to $^1$G and $^3$G have their wavelengths significantly changed in the correlated calculations, by about 780 Å and 310 Å, respectively. Both 3s8g $^1$G and 3s8g $^3$G are heavily perturbed by 3p4f from below, but the singlet is also affected by 3d$^2$ $^1$G which pushes 3p4f $^1$G closer to 3s8g $^1$G and therefore increases the perturbation. In Cl VI this large effect has disappeared since 3d$^2$ is now too far away in energy and the major perturbation is now from 3p5f instead. In Ar VII
this perturbation has become very large and the wavelengths are decreased by 340 Å. We now follow the 3s6g–3s7h transitions in the same way. In S V both transitions have their wavelengths decreased in the correlated calculations due to 3p4f which is perturbing 3s6g from above. 3s6g 1G is also perturbed from below by 3d2 1G producing a gap of about 180 Å.
between the two transitions. In Cl VI both transitions have a longer wavelength since 3p4f is now perturbing from below. Even though 3d2 is now further away in energy, there is a larger gap between the two transitions. This is because 3d2 is not only perturbing 3s6g 1G, but is also pushing 3p4f 1G closer in energy, resulting in a greater interaction between the two terms. In Ar VII this perturbation has become very small and both transitions have similar wavelengths.

Finally, we look at the 3s5g–3s6h transitions where there are no major changes along the sequence. The interesting effect here is that in S V the wavelengths of the 3s5g 1G–3s6h 1,3H transitions are shorter than the 3s5g 3G–3s6h 1,3H transitions, but in Ar VII the order is reversed.

4.3. O V

As a further test of our method, we calculated the lifetimes of the four heavily perturbed 2s6g 1,3G levels in O V (see section 2.4) to compare with the experimental values of Kink et al (1999). Table 6 shows that there is good agreement with the experimental lifetimes. These results add further confidence in the layered method as a good technique for investigating perturbed Rydberg states.

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