**Astronomy
&
Astrophysics**

Accurate calculation of oscillator strengths for Cl II lines using non-orthogonal wavefunctions[*]

S. S. Tayal

Department of Physics, Clark Atlanta University, Atlanta, GA 30314, USA

Abstract. Non-orthogonal orbitals technique in the multiconfiguration Hartree-Fock approach is used to calculate oscillator strengths and transition probabilities for allowed and intercombination lines in Cl II. The relativistic corrections are included through the Breit-Pauli Hamiltonian. The Cl II wave functions show strong term dependence. The non-orthogonal orbitals are used to describe the term dependence of radial functions. Large sets of spectroscopic and correlation functions are chosen to describe adequately strong interactions in the $3s^2 3p^3 nl$ $^3P^o$, $^1P^o$ and $^3D^o$ Rydberg series and to properly account for the important correlation and relaxation effects. The length and velocity forms of oscillator strength show good agreement for most transitions. The calculated radiative lifetime for the $3s3p^5$ $^3P^o$ state is in good agreement with experiment.

Key words. atomic data – atomic processes – line: formation

1. Introduction

Emission lines of Cl II are detected at optical and ultraviolet wavelengths in various astrophysical plasmas. The emission features of Cl II are observed in the spectra of the Io torus from both ground-based (Küppers & Schneider 2000) and Far-Ultraviolet Spectroscopic Explorer (FUSE) (Feldman et al. 2001) observations. The Cl II lines are also identified in the high-resolution spectrum of the symbiotic star RR Telescopii as well as in the spectra of the planetary nebulae NGC 6741 and IC 5117 (Keenan et al. 2003). The oscillator strengths and transition probabilities of allowed and intercombination lines in Cl II are needed for the determination of diagnostic line ratios that can subsequently be compared to astrophysical observations.

Previously Deb et al. (2003) reported oscillator strengths for some allowed transitions between low-lying fine-structure levels. They used structure code CIV3 (Hibbert 1975; Glass & Hibbert 1978) in their configuration-interaction (CI) calculations. They utilized a set of orthogonal spectroscopic and correlation orbitals to construct CI wavefunctions of the fine-structure levels belonging to the $3s^2 3p^4$, $3s3p^5$, $3s^2 3p^3 3d$, $3s^2 3p^3 4s$ and $3s^2 3p^3 4p$ configurations. The R-matrix method (Berrington et al. 1995) in the LS coupling scheme has been used by Berrington & Nakazaki (2002) to calculate radiative atomic data such as excitation energies, oscillator strengths and ground state photoionization cross sections for chlorine atom and its ions. More recently, Tayal (2003) investigated the term dependence of one-electron radial functions and strong interactions in the different $^3P^o$, $^1P^o$ and $^3D^o$ Rydberg series.

The importance of various correlation corrections was also examined and it was found that Cl II wavefunctions exhibit significant core-valence correlation or core polarization for the outer electron. The other earlier studies include the calculations of Fawcett (1986) and Biemont & Hansen (1986) who used Slater integrals as variable parameters to minimize the discrepancies between the computed and measured energy levels. Biemont & Hansen (1986) and Mendoza & Zeippen (1983) reported radiative transition probabilities of forbidden transitions in the ground $3s^2 3p^4$ configuration. Fawcett (1986) reported energy levels and oscillator strengths for the $3s^2 3p^4$–$3s3p^5$, $3s^2 3p^4$–$3s^2 3p^3 3d$ and $3s^2 3p^4$–$3s^2 3p^3 4s$ transitions.

The measurement of lifetimes of the $3s3p^5$ $^3P^o$ levels has been reported by Bashkin & Martinson (1971) and Lawrence (1969). Bashkin & Martinson (1971) used the beam-foil technique and Lawrence (1969) used a pulsed-electron technique to measure the lifetimes of the $3s3p^5$ $^3P^o$ excited levels. Because of the need of accurate oscillator strengths for allowed and intercombination lines of Cl II in a reliable and sophisticated approximation, we extended the work of Tayal (2003) to include relativistic terms such as mass correction, Darwin term, spin-orbit, spin-other-orbit and spin-spin interactions in the Breit-Pauli Hamiltonian. It may be noted that significant mixing between a number of Cl II levels is caused by spin-orbit interaction in intermediate coupling. The diagonalization of the Hamiltonian matrix gives eigenfunctions of the total angular momentum J and parity π.

2. Computational details

We used non-orthogonal orbitals to represent different Cl II states. The non-orthogonal orbitals provide much greater flexibility in the choice of wavefunctions than the orthogonal

---

[*] Tables 1 to 4 are only available in electronic form at the CDS via anonymous ftp to `cdsarc.u-strasbg.fr` (130.79.128.5) or via `http://cdsweb.u-strasbg.fr/cgi-bin/qcat?J/A+A/426/717`

orbitals and also allow to include correlation with a reasonable number of configurations and correlated orbitals (Zatsarinny & Tayal 2001). Our calculations are performed using the multi-configuration Hartree-Fock (MCHF) method (Froese Fischer 1991; Zatsarinny & Froese Fischer 1999). In the MCHF approach the atomic state is represented by an atomic state function (Brage et al. 1993)

$$\Psi(\alpha LS) = \sum_i c_i \Phi(\alpha_i LS), \tag{1}$$

where the configuration state functions $\Phi(\alpha_i LS)$ are constructed from one-electron functions and α_i defines the coupling of angular momenta of the electrons. The J-dependent atomic state functions are written as a sum over different LS values which couple to give the total angular momentum J

$$\Psi(\alpha J) = \sum_j a_j \Psi(\alpha_j L_j S_j J). \tag{2}$$

The relativistic effects are allowed by means of the Breit-Pauli operators. The intercombination transitions which only violate the LS-coupling selection rule $\Delta S = 0$ are forbidden in pure LS-coupling, but these transitions become allowed through the mixing of different LS symmetries with the same J value due to the spin-orbit interaction.

The Cl II wavefunctions exhibit large correlation corrections and strong term dependence of the one-electron orbitals. We have constructed Cl II state wavefunctions from non-orthogonal orbitals that are optimized for each atomic state separately. The low-lying states in Cl II are defined by configurations $3s^2 3p^4$, $3s3p^5$, $3s^2 3p^3 3d$, $3s^2 3p^3 4s$, $3s^2 3p^3 4p$, $3s^2 3p^3 5s$ and $3s^2 3p^3 4d$ and these states show different correlation patterns. The details of wavefunctions can be found in Tayal (2003) and here we give only a brief description. The term dependence of the valence orbitals in the $3s^2 3p^3 nl$ ($l = 0$, 1, 2) states is due to both the intermediate term and the final total term obtained by coupling the valence electron with the $3s^2 3p^3$ core. For example, the 3d orbital in the $3s^2 3p^3 3d$ $^3P^o$, $^1P^o$ and $^3D^o$ states is term-dependent with average radius in the range 2.20–5.12 au. Similarly, the 4d orbital is very term dependent with an average radius in the range 6.41–11.04 au for the $3s^2 3p^3 4d$ $^3D^o$, $^1P^o$ and $^3P^o$ states. The term dependent 5d, 6d and 7d orbitals are obtained in separate optimization for each state to represent lower members of the different $3s^2 3p^3 nd$ $^3P^o$, $^3D^o$ and $^1P^o$ Rydberg series. A set of 4s, 5s and 4p spectroscopic orbitals is obtained to describe other states considered in our work. Earlier calculations used the same set of orthogonal orbitals to represent all states of Cl II and included specific correlated orbitals to account for the term-dependence of one-electron orbitals. Members of various Rydberg series $3s^2 3p^3 nl$ display strong interaction with each other and also with the $3s3p^5$ states which can be considered as perturbers. Accurate representation of these strong mixing among different Rydberg series and perturbers is crucial for the accurate determination of oscillator strengths and transition probabilities. In addition to the spectroscopic orbitals, we obtained several correlation s, p, d and f orbitals. A set of correlated s, p, d and f orbitals are optimized on the $3s3p^5$ $^3P^o$ state. A set of three d correlation

functions was determined to accurately represent the strong interaction between the $3s^2 3p^3 (^2D^o) nd$ $^3P^o$ and $3s^2 3p^3 (^2P^o) nd$ $^3P^o$ series. Two f correlation orbitals were obtained to represent core-valence electron correlation where the valence 3d electron plays a spectator role and one of the 3p electron is excited to f orbitals. The polarization of the ground state is represented by another set of s, p, d and f correlation functions. Different sets of correlation functions were determined to describe interactions between the members of the $^3D^o$ Rydberg series and the $^1P^o$ Rydberg series and the $3s3p^5$ $^1P^o$ pertuber state. These wavefunctions are then used to calculate the length (f_L) and velocity (f_V) forms of oscillator strengths and transition probabilities for allowed and intercombination transitions among the fine-structure levels.

3. Discussion of the results

The spectroscopic and correlation functions are used to construct CI expansions for different atomic states by allowing one-electron and two-electron excitations from all the basic configurations $3s^2 3p^4$, $3s3p^5$, $3s^2 3p^3 4p$, $3s^2 3p^3 4s$, $3s^2 3p^3 3d$, $3s^2 3p^3 4d$ and $3s^2 3p^3 5s$ used in our calculation. Progressively larger calculations are performed in a systematic manner to make sure that the strong interactions between various Rydberg series and between Rydberg series and perturber states are properly accounted for. The various correlation corrections are well represented as the mean radii of correlation orbitals are comparable to the spectroscopic orbitals. In the construction of CI expansions for fine-structure levels with various J and π we used configurations generated in this excitation scheme for the atomic LS states and with insignificant configurations with coefficients less than 0.0075 omitted from the expansions. The excitation energies of fine-structure levels relative to the ground level are given in Table 1 where comparison is made with the experimental values from the National Institute of Standard and Technology (NIST) (http://physics.nist.gov). We have also included in Table 1 the difference between the present ab initio calculation and the experiment. The accuracy of calculated excitation energies on an average is about 0.005 au. The assignment and ordering of the excited levels in our calculation agrees with the experiment except for the levels of the $3s^2 3p^3 (^4S^o) 3d$ $^3D^o$ and $3s^2 3p^3 (^2D^o) 4s$ $^3D^o$ terms. The energy gap between the levels of various terms is very small.

There are strong interactions in the levels of the $^3P^o$, $^1P^o$ and $^3D^o$ Rydberg series and also between the $3s3p^5$ $^3P^o$ and $^1P^o$ perturber states with the $3s^2 3p^3 (^2D^o) nd$ $^3P^o$ and $3s^2 3p^3 (^2D^o) nd$ $^1P^o$ Rydberg series, respectively. These interactions lead to low eigenvector purities of the $3s3p^5$ $^1P^o$, $3s^2 3p^3 (^2D^o) 3d$ $^1P^o$, $3s^2 3p^3 (^2D^o) 4d$ $^1P^o$, $3s^2 3p^3 (^2P^o) 3d$ $^1P^o$, $3s3p^5$ $^3P^o$, $3s^2 3p^3 (^2P^o) 3d$ $^3P^o$, $3s^2 3p^3 (^2D^o) 3d$ $^3P^o$, $3s^2 3p^3 (^4S^o) 3d$ $^3D^o$, $3s^2 3p^3 (^4S^o) 4d$ $^3D^o$, $3s^2 3p^3 (^2D^o) 3d$ $^3D^o$ and $3s^2 3p^3 (^2P^o) 3d$ $^3D^o$ states with the main configuration contributing in the range 26–79% to the composition of states. On the other hand the members of the $3s^2 3p^3 (^2P^o) ns$ $^1P^o$, $^3P^o$ and $3s^2 3p^3 (^2D^o) ns$ $^3D^o$ Rydberg series show weak interactions with the other series of the same symmetry. However, the core correlation of the type $3s^2 3p^3 \rightarrow 3p^5$ represent large corrections for these series. In addition, one-electron virtual

excitation of one of the 3p core electrons to the correlated f orbitals also represent significant correlation effect. Some of these levels show strong interactions with each other because of their close proximity. The energy difference for some levels is negative because these excited levels are slightly over-correlated compared to the ground level in our calculation. Comparison with the calculation of Deb et al. (2003) is not made because they reported only excitation energies adjusted to experimental values after a fine-tuning to their calculated values.

The length and velocity values of oscillator strengths and length form of transition probabilities for dipole-allowed transitions between the fine-structure levels of the ground $3s^2 3p^4$ and excited $3s3p^5$, $3s^2 3p^3 3d$, $3s^2 3p^3 4s$, $3s^2 3p^3 5s$ and $3s^2 3p^3 4d$ configurations are listed in Tables 2 and 3 where our results are compared with the calculation of Deb et al. (2003) who reported oscillator strengths for some of these transitions. We have also listed the experimental wavelengths for the dipole-allowed transitions. The agreement between the length and velocity forms of oscillator strengths may to some extent indicate the accuracy of the wavefunctions and the convergence of the CI expansions. However, it is not necessarily a sufficient condition for the reliability of the results. There is normally excellent agreement between the present length and velocity forms of oscillator strengths for strong fine-structure transitions with oscillator strengths larger than 0.1. The transitions with oscillator strengths larger than 0.01 display good to excellent agreement between the length and velocity forms. Some of the transitions are very weak with very small oscillator strengths and do not show good agreement between the length and velocity values. The small oscillator strengths arise due to delicate cancellations of the dipole matrix elements in the summation of oscillator strengths. The strong mixing among several fine-structure levels may have dramatic effects on oscillator strengths. As investigated in details by Tayal (2003), the oscillator strengths of many transitions in Cl II are very sensitive to the representation of the strong interactions between various Rydberg series of the same symmetry and the Rydberg series and perturbers and to various correlation corrections. The dipole matrix elements between the main configurations comprising the initial and final states of a transition may cancel or add up resulting in small or large value of oscillator strength. For example, the strong interaction between the $3s^2 3p^3 (^2D^o) nd$ $^3P^o$ Rydberg series and $3s3p^5$ $^3P^o$ perturber state as well as between the $3s^2 3p^3 (^2D^o) nd$ $^3P^o$ and $3s^2 3p^3 (^2P^o) nd$ $^3P^o$ series have dramatic effects on the oscillator strengths for the $3s^2 3p^4$ ^3P–$3s3p^5$ $^3P^o$, $3s^2 3p^4$ ^3P–$3s^2 3p^3 (^2P^o) 3d$ $^3P^o$ and $3s^2 3p^4$ ^3P–$3s^2 3p^3 (^2D^o) 3d$ $^3P^o$ transitions. The cancellations of the dipole matrix elements for the $3s^2 3p^4$ ^3P–$3s3p^5$ $^3P^o$ and $3s^2 3p^4$ ^3P–$3s^2 3p^3 (^2P^o) 3d$ $^3P^o$ transitions give rise to small oscillator strength for these transitions and addition of dipole matrix elements for the $3s^2 3p^4$ ^3P–$3s^2 3p^3 (^2D^o) 3d$ $^3P^o$ transition gives rise to larger oscillator strength as is clear from Table 2. The correlation effect plays particularly important role for weaker transitions.

There is reasonable agreement between the present results and the calculation of Deb et al. (2003) for the $3s^2 3p^4$ $^3P_1$–$3s^2 3p^3 (^4S^o) 3d$ $^3D^o_2$, $3s^2 3p^4$ ^3P_J–$3s^2 3p^3 (^2D^o) 4s$ $^3D^o_{J'}$, $3s^2 3p^4$ ^3P_J–$3s^2 3p^3 (^4S^o) 4s$ $^3S^o_1$ and $3s^2 3p^4$ $^1D_2$–$3s^2 3p^3 (^2D^o) 4s$ $^1D^o_2$

fine-structure transitions. Our results differ significantly from the calculation of Deb et al. (2003) for other transitions. The main difference between our calculation and the calculation of Deb et al. (2003) is in the choice of radial functions and the set of configurations in the CI expansions of levels. We used term-dependent s, p and d non-orthogonal spectroscopic orbitals and several sets of s, p, d and f correlation orbitals to adequately account for various interactions and core correlation corrections. Deb et al. (2003) used same set of orthogonal spectroscopic 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p and correlation 4d, 4f, 5s, 5p, 5d radial functions to represent several levels of the $3s^2 3p^4$, $3s3p^5$, $3s^2 3p^3 3d$, $3s^2 3p^3 4s$ and $3s^2 3p^3 4p$ configurations. The most significant discrepancies between our results and the values of Deb et al. (2003) are for fine-structure transitions involving the $^3P^o$ levels. The discrepancies are caused by the inadequate treatment of the strong mixing between the levels of $^3P^o$ symmetry and the missing important core correlation corrections of the type $3s^2 3p^3 \to 3p^5$ in the calculation of Deb et al. (2003). For the accurate representation of these interactions in Cl II, the basis set of functions should not only describe the low-lying members of a Rydberg series, but also should approximate the higher bound and continuum parts of the series.

Our results for all the $3s^2 3p^4$ ^3P_J–$3s^2 3p^3 (^2P^o) 4s$ $^3P^o_{J'}$ transitions are larger than the calculation of Deb et al. (2003). The members of the $3s^2 3p^3 (^2P^o) ns$ $^3P^o$ series show weak mixing, but core correlation $3s^2 3p^3 \to 3p^5$ is significant for this series. Our results for the $3s^2 3p^4$ $^3P_2$–$3s3p^5$ $^3P^o_2$ and $3s^2 3p^4$ $^3P_0$–$3s3p^5$ $^3P^o_1$ transitions are also larger than the calculation of Deb et al. (2003). The multiplet oscillator strength for the $3s^2 3p^4$ ^3P–$3sp^5$ $^3P^o$ transition from the present work is in excellent agreement with the R-matrix calculation of Berrington & Nakazaki (2002). Our results are also supported by a good agreement with the measured lifetime for the $3s3p^5$ $^3P^o$ excited state. The calculated multiplet mean lifetime (8.48 ns) for the $3s3p^5$ $^3P^o$ excited state compares very well with the experimental lifetime of Bashkin & Martinson (7.5 ± 0.8 ns) and Lawrence (8.8 ± 0.3 ns). The largest discrepancy between our calculation and Deb et al. (2003) occurs for the $3s^2 3p^4$ ^3P_J–$3s^2 3p^3 (^2P^o) 3d$ $^3P^o_{J'}$ transitions where our results are several orders smaller than the calculation of Deb et al. (2003). The R-matrix calculation of Berrington & Nakazaki (2002) also predicted very small multiplet oscillator strength for the $3s^2 3p^4$ ^3P–$3s^2 3p^3 (^2P^o) 3d$ $^3P^o$ transition which is in reasonable agreement with our results. The composition of the $3s^2 3p^3 (^2P^o) 3d$ $^3P^o$ state in our calculation is 62.4% $3s^2 3p^3 (^2P^o) 3d$ + 27.6% $3s^2 3p^3 (^2D^o) 3d$ + 1.7% $3s^2 3p^3 (^2P^o) 4s$ + 1.6% $3s3p^5$. The leading percentage for the same state from the calculation of Deb et al. (2003) is about 80%. Clearly our calculation predicts this state to be much less pure than Deb et al. (2003) due to strong mixing and it explains to a major part the discrepancy with their calculation.

The length and velocity values of oscillator strengths and length value of transition probabilities for intercombination lines of significant strengths with oscillator strengths larger than 0.0001 are listed in Table 4. The values of oscillator strengths for intercombination lines are usually several orders of magnitude smaller than those for the allowed transitions.

However, some of the intercombination lines have comparable oscillator strengths to dipole-allowed transitions. For example, some fine-structure transitions involving higher excited $3s^23p^3(^4S^o)4d\ ^5D^o$, $3s^23p^3(^2D^o)4d\ ^1P^o$ and $3s^23p^3(^2P^o)4d\ ^1P^o$ terms have oscillator strengths larger than 0.01. The oscillator strengths for the $3s^23p^4\ ^3P_1–3s^23p^3(^4S^o)4s\ ^5S^o_2$ and $3s^23p^4\ ^3P_2–3s^23p^3(^4S^o)4s\ ^5S^o_2$ transitions are small and have values of 2.59(−5) and 5.19(−5) respectively. The intercombination lines are induced by spin-orbit interaction by causing mixing between differnt LS symmetries with the same set of quantum numbers J and π. The velocity values of oscillator strengths are listed to indicate the comparison between length and velocity values to somewhat assess the quality of wave functions. The length values should be preferred over velocity values because these remain stable with respect to the addition of more configurations. We have also shown the experimental wavelengths of intercombination lines in this table.

4. Summary

In conclusion, we have presented accurate oscillator strengths and transition probabilities of allowed and intercombination lines among the levels of the $3s^23p^4$, $3s3p^5$, $3s^23p^33d$, $3s^23p^34s$, $3s^3p^55s$ and $3s^23p^34d$ configurations. We used term-dependent non-orthogonal orbitals for the construction of CI wavefunctions for these levels. Different sets of spectroscopic and correlation orbitals are used to adequately describe the interactions between various Rydberg series and Rydberg series and perturber states. The wavefunctions display large correlation corrections. The calculated energies and lifetime for excited states show good agreement with the measured values. There is good agreement between the length and velocity values of oscillator strengths for most lines. Significant discrepancies with available oscillator strengths are noted for some transitions. Our oscillator strengths should be useful to model astrophysical plasmas and to interpret the recent ground-based and FUSE observations.

References

Bashkin, S., & Martinson, I. 1971, J. Opt. Soc. Am., 61, 1686
Berrington, K. A., Eissner, W. B., & Norrington, P. H. 1995, Comput. Phys. Commun., 92, 290
Berrington, K. A., & Nakazaki, S. 2002, At. Data Nucl. Data Tables, 82, 1
Biemont, E., & Hansen, J. E. 1986, Phys. Scr., 34, 116
Brage, T., Merkelis, G., & Froese Fischer, C. 1993, Phys. Lett. A, 174, 111
Deb, N. C., Crothers, D. S. F., Felfli, Z., & Msezane, A. Z. 2003, J. Phys. B, 36, L47
Fawcett, B. C. 1986, At. Data Nucl. Data Tables, 35, 185
Feldman, P. D., Thomas, B. A., Berman, A. F., et al. 2001, ApJ, 554, L123
Froese Fischer, C. 1991, Comput. Phys. Commun., 64, 369
Glass, R., & Hibbert, A. 1978, Comput. Phys. Commun., 16, 19
Hibbert, A. 1975, Comput. Phys. Commun., 9, 141
Keenan, F. P., Aller, L. H., Exter, K. M., Hyung, S, & Pollacco, D. L. 2003, ApJ, 584, 385
Küppers, M. E., & Schneider, N. M. 2000, Geophys. Res. Lett., 27, 513
Lawrence, G. M. 1969, Phys. Rev., 179, 134
Mendoza, C., & Zeippen, C. J. 1983, MNRAS, 202, 981
Tayal, S. S. 2003, J. Phys. B, 36, 3239
Zatsarinny, O., & Froese Fischer, C. 1999, Comput. Phys. Commun., 124, 247
Zatsarinny, O., & Tayal, S. S. 2001, J. Phys. B, 34, 3383