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Influence of relaxation effects on probabilities of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ intercombination transitions in NII*

Yuan Ping(袁 萍)[a)b)], Liu Xin-Sheng(刘欣生)[b)] Xie Lu-You(颉录有)[a)],
Zhang Yi-Jun(张义军)[b)], and Dong Chen-Zhong(董晨钟)[a)]

[a)] *College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou 730070, China*
[b)] *Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Science, Lanzhou 730000, China*

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Transition probabilities of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ intercombination transitions in NII have been calculated by using a large-scale multiconfiguration Dirac–Fock method. In the calculation the most important effects of relativity, correlation, and relaxation are considered. From the calculated transition probabilities, the lifetime of the $2s2p^3\ ^5S_2$ metastable state is derived. The result is in excellent agreement with the latest experimental result. In the meantime the influence of anomalously strong relaxation effects on probabilities of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ lines in NII have been found.

Keywords: transition probability, lifetime, multiconfiguration Dirac–Fock method
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1. Introduction

Nitrogen is among the most abundant elements on the earth and stars. Knowledge of the spectrum of singly ionized nitrogen is essential both for plasma diagnostics and for a better understanding of the Earth's ionosphere and similar plasmas elsewhere in the solar system. Auroral spectra, for example, excited by particle bombardment of the upper atmosphere, show an emission feature near 214 nm. This emission was first identified as belonging to the radical NO, but was later found to be mainly of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ intercombination transitions of NII. So the properties of these transitions and the $2s2p^3\ ^5S_2$ metastable state have attracted considerable interest both in theoretical and experimental fields during the previous two decades.[1−9] On the experiment side, different devices have been used to measure the lifetime of the $2s2p^3\ ^5S_2$ state: Knight[1] carried out the early experiment on radio-frequency ion trap and gave the result of 4.2±0.6 ms. Using an electrostatic ion trap, Calamai and Johnson[2] obtained the lifetime of 5.4±0.3 ms. Working with a heavy-ion storage ring, Träbert *et al*[3] achieved the latest experimental result so far, 5.88±0.03 ms. There were also many theoretical studies subsequently corroborated experimental conclusion qualitatively.[4−9] Using MCDF method, Cowan *et al*[6] calculated the transition probabilities of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ lines and obtain the value of 3.2±1.6 ms for the lifetime of the $^5S_2$ state. More recently, Hibbert[9] performed an extensive calculation with the CIV3 code, and gave the result of 5.43±0.3 ms. Although the calculated lifetimes helped reconcile the origin of the 214 nm auroral feature, and supported the role of this state in the auroral emission, remarkable discrepancies between them existed — the earlier calculated lifetimes differed from each other by as much as 50%, and also had an obvious deviation from experimental values.

In practical calculations, the accuracy for calculated lifetimes depends on the accuracy of the relevant transition probability. To obtain transition probability values with a sufficient precision, large wavefunc-

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tion expansions are often needed.[10] For *ab initio* calculations, these wavefunctions must include the most dominant physical effects of relativity, electron correlations, and relaxation (the rearrangement of the electron density caused by emitting photons) within a common framework. The state $2s2p^3\ ^5S_2$ is the lowest excited state above the $2s^22p^2$ ground configuration of NII ion, it mixes with the $^3P_2$, $^3D_2$ and $^1D_2$ levels of the $2s2p^3$ configuration, which opens up the electric-dipole ($E1$) intercombination decay channels to the $2s^22p^2\ ^3P_{1,2}$ levels and also (weakly) to the $2s^22p^2$ $^3D_2$, $^1D_2$ levels.[4] Accurate calculation on these transitions is very cumbersome as complex configurations mixing is important to energy levels, and their transition probabilities are very sensitive to the influence of various effects such as, relativity, correlation, and especially relaxation.[11] Although the importance of relaxation effect is already well established,[12] this effect has so far been included only in a few studies of transition probabilities. Since, in practice, it requires the inclusion of a large number of non-vanishing overlaps of orbital functions of the same symmetry, which make the calculation very complicated. The previous work on $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ transitions of NII did not include these effects particularly, so it could not treat their influence efficiently.

There have been many methods and works on atomic structure calculations in recent years.[13,14] The newly revised program REOS99 [15] accounts for all of these effects systematically for the computation of Einstein coefficient. It applies relativistic wavefunctions from the GRASP92 package,[16] which need subsequently be expanded into determinant basis. With this code, transition probabilities for the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ electric-dipole ($E1$) intercombination transitions in NII have been calculated to obtain the lifetime of the $2s2p^3\ ^5S_2$ metastable state. The result is in excellent agreement with the latest experimental data.

In the meantime, the influence of anomalously strong relaxation effects on probabilities of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ intercombination transitions have been found.

2.Computing method

To calculate the level energies and transition probabilities, wavefunctions have been generated by the GRASP92 structure code which is an implementation of the multi-configuration Dirac–Fock (MCDF) method. In MCDF model, an atomic state wavefunction (ASF) with total angular momentum J and parity P is written as a linear combination of the configuration state wavefunctions (CSFs) of the same symmetry

$$|\alpha(PJM)\rangle = \sum_{r=1}^{n_c} C_r(\alpha)|\Gamma_r(PJM)\rangle, \qquad (1)$$

where n_c is the number of CSF, it reflects the extent to which electron correlations are taken into account, and $C_r(\alpha)$ is the configuration mixing coefficient corresponding to each single CSF $|\Gamma_r(PJM)\rangle$. These CSFs are further expressed by all possible Slater determinants in each corresponding configuration

$$|\Gamma_r(PJM)\rangle = \sum_p B_{rp}|\Psi_p\rangle, \qquad (2)$$

where B_{rp} is the expansion coefficient, and $|\Psi_p\rangle$ is the N-particle Slater determinant, which can be constructed from an orthonormal set of single-electron orbitals $\psi_{n\kappa\mu}$. Further relativistic corrections to the electron–electron interactions are added by diagonalizing the Dirac–Coulomb–Breit Hamiltonian matrix. The dominant quantum electrodynamic contributions, i.e. self-energy and vacuum polarization effect, also have been included in the computations of the total energy as a perturbation.

In calculations, we categorized the levels concerned, according to their symmetry J^p, into three groups — one for $2s\ 2p^3\ ^5S_2$ ($J^p = 2^-$), the second for $2s^2\ 2p^2\ ^3P_1$ ($J^p = 1^+$), and the third for $2s^2\ 2p^2\ ^3P_2$ ($J^p = 2^+$). We choose $\{2s2p^3 + 2s^22p3s + 2s^22p3d + 2s2p^23p\}$ and $\{2s^22p^2 + 2s^22p3p + 2p^4 + 2s2p^23s\}$ as reference configurations for the odd parity levels and even parity levels respectively, so as to carry out a separate optimization procedure using an extended optimal level (EOL) model of GRASP92. In order to include CSFs in the expansion of the wavefunctions as many as possible, namely to take into account the correlation effects more effectively, the active space method, which was presented at first in quantum chemistry, was used to generate the configuration state list , and then the systematically enlarged MCDF method was adopted to extend the CSFs gradually and carry out a many-step optimization until achieving the levels and wavefunctions with sufficient accuracy.

The Einstein spontaneous emission probability for transition from upper state β to lower state α can be given by

$$A_{\beta\alpha} = \frac{2\pi}{2j_\beta + 1} \sum_{M_\beta} \sum_{M_\alpha} |M_{\beta\alpha}^{(L)}|^2, \tag{3}$$

where j_β is the total angular momentum of the state β, and $M_{\beta\alpha}$ is the transition matrix. The latter can be calculated by

$$\begin{aligned} M_{\beta\alpha}^{(L)} =& \langle \alpha(P_\alpha J_\alpha M_\alpha)|O^{(L)}|\beta(P_\beta J_\beta M_\beta)\rangle \\ =& \sum_{r,s} C_r(\alpha) C_s(\beta) \langle \Gamma_r(P_\alpha J_\alpha M_\alpha)|O^{(L)}| \\ & \times \Gamma_s(P_\beta J_\beta M_\beta)\rangle, \end{aligned} \tag{4}$$

where $O^{(L)}$ is the tensor operator of radiation electromagnetic field with rank L.

When considering relaxation effect , two sets of electron orbital from the initial and final atomic states are no longer strictly orthogonal. In this paper, a new program REOS99 has been adopted to account for this effect systematically.

We assume $\langle \psi_k|\psi_l\rangle = \langle \varphi_k|\varphi_l\rangle = \delta_{kl}$ for each set of orbitals but $\langle \psi_k|\varphi_l\rangle = d_{pq}(kl)$ for the cross overlap products with $\langle \psi_k|\varphi_k\rangle \approx 1$. In this approximation, the total overlap of two determinants corresponding to initial and final states of the transition are expressed by $D_{pq}(kl) = \langle \Psi_p|\Phi_q\rangle = \det\{d_{pq}(kl)\}$ Then the matrix element in Eq.(4) can be further expressed as

$$\begin{aligned} & \langle \Gamma_r(P_\alpha J_\alpha M_\alpha)|O^{(L)}|\Gamma_s(P_\beta J_\beta M_\beta)\rangle \\ =& \sum_{p,q} \sum_{k,l} B_{rp} B_{sq} \langle \psi_k||O^{(L)}||\varphi_l\rangle D_{pq}(kl), \end{aligned} \tag{5}$$

where the reduced transition matrix elements $\langle \psi_k\ ||O^{(L)}||\varphi_l\rangle$ are calculated by

$$\begin{aligned} & \langle \psi_k||O^{(L)}||\varphi_l\rangle \\ =& \left(\frac{(2j_l+1)\omega}{\pi c}\right)^{1/2} (-1)^{j_l - 1/2} \begin{pmatrix} j_k & L & j_l \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \overline{M}_{kl}. \end{aligned} \tag{6}$$

Here $\overline{M}_{kl}$ is the radial integral, which has different expressions for various types of transitions ($E1$, $M1$, $E2$, $M2$). For $E1$ transition, it is usually calculated in Babushkin and Coulomb gauges, corresponding to the length and velocity forms respectively, and the agreement between different gauges can be used as a test of the quality of the wavefunctions.

3. Results and discussion

The influence of relaxation effect plays a crucial role in the calculation of transition probabilities , especially for intercombination transitions of low-ionized ions.[4] In order to show in details the influence of relaxation effects on the transition probabilities concerned. Table 1 list the calculated wavelengths and probabilities of the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ $E1$ intercombination transitions, where the transition probabilities are presented in length and velocity gauges separately. For each transition, two different cases, namely with and with out relaxation approximations have been considered. To exclude the influence of the theoretical energy levels on the transition probabilities, the corresponding experimental wavelengths are used in the calculations. Since the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ transitions are very weak lines, the values of their probabilities are very small and sensitive to various factors. As is seen from Table 1, the influence of relaxation effects on them are very remarkable: in the case of without relaxation, the result are almost incorrect, and furthermore, the agreement between length and velocity gauges is also quite poor, their discrepancy are of 1–2 orders of magnitude. Such a large error is mainly due to the obvious difference between the orbitals of the final state with stable closed shell $2s^2$, open shell $2p^2$ and the initial state with open shell $2s2p^3$, which influences the transition probabilities seriously. When the relaxation effects have been taken into account, a great improvement is achieved, the calculated and observed wavelengths agree within 0.02%, and the probabilities in length and velocity gauges agree with each other to 2%. There are no theoretical and experimental data available on transition probabilities so far to confirm the accuracy achieved in our calculations, Table 2 displays the calculated lifetime[17] of the $2s2p^3\ ^5S_2$ state that is mainly derived from the $2s2p^3\ ^5S_2$–$2s^22p^2\ ^3P_{1,2}$ transition probabilities. For comparison, the measured and previous calculated results available are also listed. As shown in Table 2, the present result is preferable, the calculated lifetime (5.84 ms) agrees with the latest experimental result [3] to 1%.

Table 1. Wavelengths (in nm) and transition probabilities A (in s^{-1}) of the $2s2p^3\ {}^5S_2$–$2s^22p^2\ {}^3P_{1,2}$ lines in NII.

Transition	λ_{cal}	λ_{exp}[3]	With relaxation		Without relaxation	
			A_l	A_v	A_l	A_v
			a[b]	a[b]	a[b]	a[b]
$^5S_2$–$^3P_1$	214.015	214.0	4.89015(1)	4.79260(1)	3.27070(5)	3.78468(6)
$^5S_2$–$^3P_2$	214.432	214.4	1.22166(2)	1.23388(2)	5.62947(6)	1.11469(8)

$a(b)$ denotes $a \times 10^b$

A_l denotes the transition probabilities in length gauge, A_v denotes transition probabilities in velocity gauge.

Table 2. Lifetime value for the $2s2p^3\ {}^5S_2$ level, compared with previous computations and experimental results.

	τ/ms	Ref.
Theory		
	6.4	[4]
	5.8	[5]
	3.2±1.6	[6]
	6.45	[7]
	5.43±0.3	[8,9]
	5.84	This work
Experiment		
	4.2±0.6	[1]
	5.4±0.3	[2]
	5.88±0.03	[3]

In conclusion, we have calculated the transition probabilities of the $2s2p^3\ {}^5S_2$–$2s^22p^2\ {}^3P_{1,2}$ intercombination transitions in NII and found the influence of unusually strong relaxation effects on the probabilities in this paper. The calculation shown in this paper might be used to test the different theoretical methods of atomic structure. On the other hand, useful reference data are provided for studies of other forbidden transitions like the solar coronal lines, and for further astrophysical investigations.

References

[1] Knight R D 1982 *Phys. Rev. Lett.* **48** 792

[2] Calamai A G and Johnson C E 1991 *Phys. Rev.* A **44** 218

[3] Träbert E *et al* 1998 *Phys. Rev.* A **58** 4449

[4] Hibbert A and Bates D R 1981 *Planet. Space Sci.* **29** 263

[5] Dalgarno A, Victor G A and Hartquist T W 1981 *Geophys. Res. Lett.* **8** 603

[6] Cowan R D, Hobbs L M and York D G 1982 *Astrophys. J.* **257** 373

[7] Bell K L, Hibbert A and Stafford R P 1995 *Phys. Scr.* **52** 240

[8] Hibbert A 1996 *Phys. Scr.* T **65** 104

[9] Brage T, Hibbert A and LeckRone D S 1997 *Astrophys. J.* **478** 423

[10] Fritzsche S, Dong C Z and Träbert E 2000 *Mon. Not. R. Astron. Soc.* **318** 263

[11] Dong C Z, Fritzsche S *et al* 2001 *Phys. Scr.* T **92** 294

[12] Fritzsche S and Grant I P 1994 *Phys. Lett.* A **186** 152

[13] Gou B C, Deng W S and Zhang J P 1998 *Chin. Phys.* **7** 561

[14] Sheng Y, Zhu Z H, Wang R and Jiang G 2001 *Chin. Phys.* **6** 505

[15] Fritzsche S, Fischer C F and Dong C Z 2000 *Compt. Phys. Commun.* **124** 340

[16] Parpia F A, Fischer C F *et al* 1996 *Comput. Phys. Commun* **94** 249

[17] Yuan P, Liu X S, Zhang Y J, Xie L Y and Dong C Z 2002 *Acta Phys. Sin.* **51** 2495 (in Chinese)