

H, He-like recombination spectra VI: quadrupole l -changing collisions

E. Deliporanidou^{1,2}★, N. R. Badnell,¹ P. J. Storey,³ G. Del Zanna^{2,4} and G. J. Ferland⁵

¹*Department of Physics, University of Strathclyde, Glasgow G4 0NG, UK*

²*DAMTP, Centre for Mathematical Sciences, University of Cambridge, Wilberforce Road, Cambridge CB3 0WA, UK*

³*Department of Physics and Astronomy, University College London, London WC1E 6BT, UK*

⁴*School of Physics and Astronomy, University of Leicester, Leicester LE1 7RH, UK*

⁵*Department of Physics and Astronomy, University of Kentucky, Lexington, KY 40506, USA*

Accepted 2025 April 9. Received 2025 April 9; in original form 2025 February 27

ABSTRACT

We have developed a simple analytic formula that well describes quadrupole l -changing collisions of the form $nl \rightarrow nl'$, as confirmed by comparison with numerical quantal Born calculations obtained with the program AUTOSTRUCTURE. Such formulae could easily be included in models of astrophysical plasma emission, such as the hydrogen and helium-like recombination spectra. When compared with the results of previous quantal calculations based upon an analytic solution of the time-dependent Schrödinger equation by Vrinceanu & Flannery, we find relatively good agreement, with the exception of large $l > n/2$ transitions. We provide a tentative explanation for such discrepancies. However, we also show that the rates for quadrupole l -changing collisions are typically two orders of magnitude lower than the dipolar ones. Inclusion of the quadrupolar rates in a hydrogenic collisional-radiative model of nebular plasma shows minimal changes to the level populations, typically within 1 per cent in nebular conditions. Simple and complete theories are now available for l -changing collisions suitable for astrophysical applications.

Key words: atomic data – ISM: abundances – H II regions – cosmology: observations – primordial nucleosynthesis.

1 INTRODUCTION

Astrophysical plasma, comprising 95 per cent of cosmic baryonic matter, consists of a mixture of ions, atoms, and free electrons and protons. Given the large abundance of hydrogen and helium, accurate non-LTE collisional-radiative modelling including several ionization and recombination processes is required for a vast amount of astrophysical applications. Long ago, it was recognized that dipole l -changing collisions by protons and electrons are fundamentally important for such models (Pengelly & Seaton 1964). l -changing collisions are also generally important for redistributing the populations of atomic states of any atom. For this reason, there has been recent interest in improving upon the seminal work of Pengelly & Seaton (1964), see our previous paper (Badnell et al. 2021) and references therein.

This paper focuses on quadrupole l -changing collisions for hydrogen, addressing the need for an investigation that is presently absent in the literature. Such collisions are of the form $nl \rightarrow nl'$, where $|l - l'| = \Delta l = 2$ and for which we can neglect the excitation energy ($\Delta E \approx 0$). In paper II of this series by Guzmán et al. (2017), the effects of higher multipole l -changing collisions were briefly examined using the simplified semiclassical (SSC) method of Vrinceanu, Onofrio & Sadeghpour (2012) for He-like ions, see Section 2.4. It was found that while multipole effects are generally negligible, they can contribute up to 50 per cent of the differences

between the Quantum Mechanical (QM), see Section 2.3, and the Pengelly & Seaton (1964) method (PSM) results, for certain Brackett and Paschen lines at common astrophysical densities. Notably, these differences in line intensities do not exceed 2 per cent. In this paper we extend this investigation to quadrupole l -changing collisions for hydrogen, by providing an analysis of their impact. As in paper II, we explore the role of different approximations and examine the significance of quadrupole transitions under relevant conditions.

The time-dependent Schrödinger equation (TDSE) quantum mechanical (QM) approximation and the Born approximation are the primary tools that can be used to solve quadrupole l -changing collisions. An initial comparison between the two reveals a discrepancy, particularly at large $nl \rightarrow nl'$ transitions. Consequently, a deeper analytical comparison was undertaken, employing two additional rate coefficient expressions representing accurate TDSE QM and Born approximations to search for the root causes of the observed disagreement. The Born approximation is a well-known QM approximation for higher multipole expansions. The SSC approximation developed by Vrinceanu et al. (2012) and a rate coefficient expression developed by Burgess & Tully (2005) constitute the TDSE QM and the Born approximations, respectively. Both expressions necessitate simplifications and modifications to account for quadrupole l -changing collisions effectively.

In Section 2, we discuss the Born and QM rate coefficients. In Section 3, we discuss the methods we used for the study. In Section 4, we present the outcomes of the numerical evaluation and analytic comparison, identifying agreements and discrepancies between the approximations. In Section 5, we discuss the applications of our

* E-mail: ed650@cam.ac.uk

analysis by testing the relevance of quadrupole rates. In Section 6, we elaborate on the outcomes of the numerical analysis.

2 THEORY

The key quantity used for collisional radiative modelling is the rate coefficient [$\text{cm}^3 \text{s}^{-1}$] (see e.g. Burgess & Tully 2005)

$$q_{i \rightarrow j} = \int f(v) v Q_{ij} dv, \quad (1)$$

where $f(v)$ is the velocity distribution of the free particles, assumed to be Maxwellian (a generally good approximation for astrophysical plasma), and Q_{ij} is the cross-section for the l -changing collisions between the target states i and j .

The high-energy scattering regime of atoms is characterized by the ratio $E/\Delta E$, where E represents the thermal energy and ΔE is the excitation energy. This regime requires a large ratio, meaning the thermal energy significantly exceeds the excitation energy. Quadrupole l -changing collisions exhibit an energy dependence when ΔE is finite. When $E/\Delta E$ becomes large, the regime approaches an infinite energy limit, effectively making the cross-section independent of scattering energy. This limit, in which $\Delta E \rightarrow 0$, was detailed by Burgess & Tully (2005) in their study of low- l proton–electron collisions involving fine-structure excitations with zero excitation energy.

The electric quadrupole radiation is much weaker than the electric dipole radiation. In quadrupole proton–electron collisions within a hydrogen atom, the proton changes the electron’s angular momentum by 2 units due to angular momentum exchange. Without a cut-off parameter, the cross-section for dipole l -changing collisions would diverge. However, quadrupole cross-sections do not diverge, so no cut-off is necessary.

The interactions asymptotically vary as $1/r^2$ for the dipole, and as $1/r^3$ for quadrupole l -changing collisions.

2.1 The Born approximation

The Born approximation treats the collider as a plane wave. The total cross-section is obtained by summing over a multipole expansion. For scattering between atoms and electrons, the Born cross-section as coded by NRB within AUTOSTRUCTURE (Badnell 2011) is widely used. The calculations follow the descriptions given for the different types of transitions by Burgess, Chidichimo & Tully (1997) and Chidichimo, Badnell & Tully (2003), which refer to the original works by Born (1926) and Bethe (1930).

The Born approximation is well-suited to describing proton–ion collisions, especially quadrupole l -changing collisions. We present the full Born approximation for quadrupole l -changing collisions in Appendix A. This was derived by NRB based on the above papers, using further assumptions and approximations to make it suitable for quadrupole l -changing collisions. The final Born cross-section expression is given by

$$Q_{nl \rightarrow n'l'}^{\text{Born}} = \frac{\pi}{K_q^2 (2l+1)} \times 8 \int \frac{dK}{K^3} 4\pi \sum_{\lambda} | \langle l' \| \mathbf{B}_{\lambda} \| l \rangle |^2, \quad (2)$$

where the collision strength is the integral over the momentum transfer, given by

$$\Omega_{nl \rightarrow n'l'}^{\text{Born}} = 8 \int \frac{dK}{K^3} 4\pi \sum_{\lambda} | \langle n'l' \| \mathbf{B}_{\lambda} \| nl \rangle |^2, \quad (3)$$

and, $| \langle n'l' \| \mathbf{B}_{\lambda} \| nl \rangle |^2$ is the term in the summation for multipole

$$\begin{aligned} \langle n'l' \| \mathbf{B}_{\lambda} \| nl \rangle &= (-1)^{l'} \left[\frac{(2l+1)(2\lambda+1)(2l'+1)}{4\pi} \right]^{1/2} \\ &\times \begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0 \end{pmatrix} \langle l' \| \mathbf{j}_{\lambda} \| l \rangle, \end{aligned} \quad (4)$$

where the 3- j symbol is equal to 0, unless the sum of the terms is even and $|l-l'| \leq \lambda \leq (l+l')$, based on the triangular rule of the Wigner 3- j symbol that determines the allowed multipoles of the Born approximation. K_q is the initial momentum of the free electron, K is the momentum transfer, and λ indicates the multipole.

The 3- j symbol also mirrors the conservation of parity during interactions, influencing the progression of alternating multipole sequences. In cases of parity conservation, transitions between angular momenta l and l' yield electric multipole series in the form $1-3-5-7$ or $2-4-6-8$, determined by the parity of the electric multipole operator, represented as $(-1)^{\lambda}$.

The radial part of the cross-section integral involves a spherical Bessel function as presented below,

$$\langle l' \| \mathbf{j}_{\lambda} \| l \rangle = \int_0^{\infty} P_{n'l'}(r) [j_{\lambda}(Kr) - \delta_{\lambda 0}] P_{nl}(r) dr. \quad (5)$$

There is no analytic expression for the integral of the spherical Bessel function between two wave functions, even for hydrogen. Burgess & Tully (2005) developed simple expressions for proton–electron collisions, which are similar to Born for l -changing collisions, as the excitation energy is zero and the collision strength is a constant.

2.2 Burgess and Tully modified Born (BTM)

Burgess & Tully (2005) gave an analytic approximation to the full Born cross-section for the general case ($\Delta E \neq 0$) which we denote BT, but it depended on a numerical quadrupole line strength (S_2) and an effective target radius (r_0), the latter to be determined by matching to numerical Born results. Their expression was initially provided for modelling proton collisions. They obtained cross-sections, collision strengths, and rate coefficients with accurate behaviour at infinite energies and higher temperatures, correcting earlier mistakes. As we wanted to obtain an analytic expression for our comparisons, we have specialized their approach to the $\Delta E = 0$ case. We denote this as the modified Burgess–Tully (BTM) method.

The BTM rate coefficient, q^{BTM} , is related to the collision strength Ω^{BTM} via

$$q_{nl \rightarrow n'l'}^{\text{BTM}} = \frac{2}{\omega_l} \left(\frac{\pi I_H}{kT} \right)^{1/2} \mu^{-3/2} \Omega_{nl \rightarrow n'l'}^{\text{BTM}} \exp(-E/kT) \frac{a_0^3}{\tau_0}, \quad (6)$$

where $\omega_l = 2l+1$, is the statistical weight, $\mu = M/m_e$ is the dimensionless reduced mass, $\sqrt{M} = 30.31$ and $k = 6.33 \times 10^{-6}$ [Ryd K^{-1}] in atomic units. E is the excitation energy which is zero, and hence, $\exp(-E/kT) = 1$. Burgess & Tully (2005) introduce a quantity Y_{ij} (equation 35) in their rate coefficient expression (equation 34), however, the quantity Y_{ij} is equal to the collision strength Ω_{ij} , because Ω^{BTM} is independent of energy.

The quadrupole Born collision strength in its high-energy form is given by

$$\Omega_{nl \rightarrow n'l'}^{\text{BTM}} = \frac{4}{5} \left(\frac{\mu Z_p}{r_0} \right)^2 S_2(nl - n'l'), \quad (7)$$

where Z_p is the charge number of the projectile, S_2 is the quadrupole line strength, and r_0 is the effective target radius

(Burgess & Tully 2005). The BT expression used the Bethe approximation and quadrupole line strength from the literature. Their work is focused on proton excitation of the fine structure of the ground term in complex ions, as opposed to the l -changing collisions in Rydberg hydrogen, which are effectively degenerate. The high energy limit of the BT formalism corresponds to the $\Delta E = 0$ modification in the BTM expression.

An analytic form for S_2 does not appear to be readily available in the literature. We have used the ladder operator techniques of Hey (2006) to obtain one:

$$S_2 = \left(\frac{300}{2}\right) \left(\frac{n}{2Z_t}\right)^4 \left(\frac{l_{>}(l_{>} - 1)}{(2l_{>} - 1)}\right) (n^2 - l_{>}^2)(n^2 - (l_{>} - 1)^2), \quad (8)$$

where Z_t is the charge number of the target, and $l_{>} = \max(l, l')$ (see details in Appendix B). We have verified this expression against the numerical results from AUTOSTRUCTURE.

For the effective target radius r_0 , we adopt an expression of the form

$$r_0 = \frac{c_0 n^2}{Z_t}, \quad (9)$$

obtained based on the turning points of the asymptotic behaviour of the bounded and unbounded solutions of the Schrödinger's radial equation, as $r \rightarrow \infty$.

We find the best agreement between our analytic approximation and exact Born collision strengths if we take

$$c_0 = 1 + \left[1 - \frac{l(l+1)}{n^2}\right]^{1/4}. \quad (10)$$

If the power in equation (10) were $1/2$, then r_0 would be the outer turning point of the (hydrogenic) radial function.

2.3 TDSE

Vrinceanu & Flannery (2001) solved the TDSE for a colliding particle at large impact parameters by making use of the Stark effect in Rydberg transitions. They investigated collisions of slow charged particles at large impact parameters, and they provided an expression for the Stark mixing-transitions' probability of arbitrary angular momentum Rydberg atomic states of the form $nl \rightarrow n'l'$. This method has been evaluated for dipole l -changing collisions, but its accuracy for higher multipole collisions has not been closely reviewed yet. The TDSE quantum mechanical probability is given by Vrinceanu & Flannery (2001)

$$P_{nl \rightarrow n'l'}^{\text{QM}} = (2l' + 1) \sum_{L=|l'-l|}^{n-1} (2L+1) \left\{ \begin{matrix} l' & l & L \\ j & j & j \end{matrix} \right\}^2 \times \frac{(L!)^2 (n-L-1)!}{(n+L)!} (2 \sin \chi)^{2L} \left[C_{n-L-1}^{(L+1)}(\cos \chi) \right]^2, \quad (11)$$

where $\{...\}$ denotes a Wigner $6j$ -symbol, $C_n^{(l)}$ is an ultraspherical polynomial, and $j = (n-1)/2$. This is evaluated analytically using techniques from Edmonds (1996). The pseudo-multipole summation over L can contribute significantly in the quadrupole case, unlike the dipole case where the $L = 1$ term dominates. The rotation angle χ is written in terms of the scattering parameter α via

$$\cos \chi = \frac{1 + \alpha^2 \cos(\Delta\Phi \sqrt{1 + \alpha^2})}{1 + \alpha^2} \quad \text{and} \quad \alpha = \frac{3Z_p n \hbar}{2m_e v b}, \quad (12)$$

where $\Delta\Phi = \pi$, b is the impact parameter and v is the projectile speed. Integration over α yields both cross-sections and rate coefficients.

Vrinceanu et al. (2012) further evaluated the TDSE QM probability term, and they re-expressed the cross-section, considering the probability dependence on the impact parameter b and the projectile velocity v , through α , which is given by

$$Q_{nl \rightarrow n'l'}^{\text{TDSE}} = \frac{9\pi}{2} \times \left(\frac{Z_p n \hbar}{m_e v}\right)^2 \times I_{l \rightarrow l'}^{(n)}, \quad (13)$$

where $I_{l \rightarrow l'}^{(n)}$ is the velocity-independent integral factor that Vrinceanu et al. (2012) introduced, which is determined by the initial and final states as

$$I_{l \rightarrow l'}^{(n)} = \int_0^\infty P_{nl \rightarrow n'l'}^{(n)}(\alpha) \frac{d\alpha}{\alpha^3}, \quad (14)$$

where the $1/\alpha^3$ dependence generates the logarithmic singularity in the cross-section for large impact parameters. It is also where the cut-off parameter is applied for dipole l -changing collisions.

The upper limit L restricts the contribution of higher multipoles in the summation of equation (11), which ultimately yields the cross-section and rate coefficient. Adjusting this limit controls the impact of higher multipoles on the numerical rate coefficient. For $l \lesssim n/2$ the 6- j symbol truncates the sum at $L = l + l'$, however, for $l \gtrsim n/2$, the upper limit $L = n - 1$ of the summation is the term that truncates the sum.

2.4 SSC

The SSC approximation is an analytic simplification of the QM approximation, without making use of the Bethe approximation and hence no cut-off parameter is introduced for the SSC. This approximation is very accurate at low impact parameters and was derived by Vrinceanu et al. (2012):

$$q_{nl \rightarrow n'l'}^{\text{SSC}} = 1.294 \times 10^{-5} \sqrt{\frac{M}{m_e}} \frac{Z_p^2}{\sqrt{T}} \times \frac{n^2 [n^2(l+l') - l_{<}^2(l+l'+2|\Delta l|)]}{(l+1/2)|\Delta l|^3} \quad [\text{cm}^3 \text{s}^{-1}], \quad (15)$$

where $l_{<}$ is the smaller of l and l' , $\sqrt{M} = 30.3039$, $m_e = 1$ in atomic units, and $Z_p = 1$.

The SSC approximation shows high accuracy on quadrupole and higher multipole l -changing collisions, compared with the old semiclassical (SC) (Vrinceanu & Flannery 2001).

3 METHODOLOGY

We employed both numerical and analytical methods to compare cross-section and rate coefficient expressions. Numerical results for the Born collision strengths are derived from AUTOSTRUCTURE. In addition, QM, SSC, and BTM cross-sections and rate coefficients are derived by a FORTRAN executable program written by NRB. The program calculates Maxwellian rate coefficients and cross-sections for approximations that describe l -changing atomic collisions. The Born rate coefficient expression is determined analytically, using the BT rate coefficient and cross-section results from the modified l -changing collisions program, and the Born collision strength results from the AUTOSTRUCTURE code, where we account for proton collisions by scaling the outputs with the $\sqrt{m_p/m_e}$ ratio.

Expressions displaying discrepancies for identical values of n and l are subjected to analytical comparison to identify the underlying

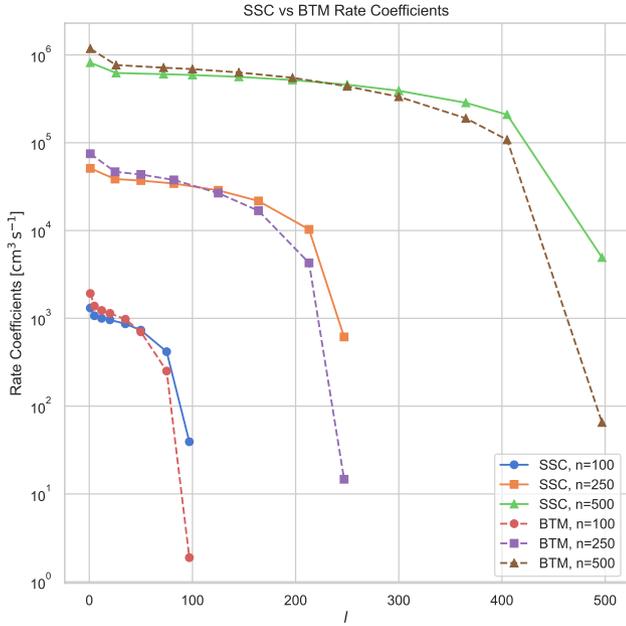


Figure 1. Variation of TDSE QM (SSC) and Born (BTM) rate coefficients [$\text{cm}^3 \text{s}^{-1}$] with l on a logarithmic scale for $T = 100$ [K].

sources of disagreement. We also investigate the contribution of higher multipoles on the summation terms of the QM and the Born approximations by restricting the contribution of higher multipoles on the Born summation and by adding an upper L limit on the QM summation and via a modification to the AUTOSTRUCTURE program.

4 RESULTS

Our numerical results reveal good agreement between rate coefficients in the range $100 < n < 500$ across all approximations for low- l , with significant discrepancies emerging at higher l values (see Fig. 1 and Table 1).

Although the Born is the most accurate approximation for the high energy behaviour, it disagrees with the TDSE QM approximation for intermediate and high l quadrupole $nl \rightarrow n'l'$ transitions. Numerical results reveal a good agreement between the BTM and the Born approximations for $c_0 = 2$.

We see from Table 1 that the SSC and BTM approximations are representative of the TDSE QM and Born results respectively over all- l . The latter two are also in good agreement with each other at low- l . However, for $l \gtrsim n/2$ we see increasing divergence between the TDSE QM/SSC and Born/BTM results. Fig. 1 shows the variation of the SSC and the BTM with l . Similarly with Table 1, there is agreement between the SSC and the BTM for small l transitions ($l \ll n$), better agreement for intermediate transitions ($l \approx n/2$) and large disagreement for $l \approx n$.

Taking the limit of intermediate- l -changing collisions ($l \ll n$) we find analytically a disagreement of approximately 0.8 when taking the ratio of $q^{\text{SSC}}/q^{\text{BTM}}$:

$$q_{nl \rightarrow n'l'}^{\text{SSC}} = 9.8 \times 10^{-6} \times n^4 \quad [\text{cm}^3 \text{s}^{-1}] \quad (16)$$

and

$$q_{nl \rightarrow n'l'}^{\text{BTM}} = 1.23 \times 10^{-5} \times n^4 \quad [\text{cm}^3 \text{s}^{-1}]. \quad (17)$$

We can see the discrepancies more clearly if we take the limit of large- l for both the BTM and SSC expressions given by equations (6) and (15) (for $Z_p = Z_t = 1$ and $T = 100$ K):

$$q_{nl \rightarrow n'l'}^{\text{BTM}} \sim 9.80 \times 10^{-5} \times l_{>}^2 \quad [\text{cm}^3 \text{s}^{-1}] \quad (18)$$

and

$$q_{nl \rightarrow n'l'}^{\text{SSC}} \sim 3.92 \times 10^{-5} l_{>}^3 \quad [\text{cm}^3 \text{s}^{-1}]. \quad (19)$$

Thus

$$q_{nl \rightarrow n'l'}^{\text{SSC}}/q_{nl \rightarrow n'l'}^{\text{BTM}} \sim 0.4 l_{>} \quad \text{as} \quad l \rightarrow n. \quad (20)$$

A full derivation of the analytic evaluation for both intermediate and large l -changing collisions is given in Appendix C.

The analytical comparison in each transition range has quantified the numerical discrepancies in the rate coefficients. We obtained additional numerical results, using the AUTOSTRUCTURE code, including an imposed restriction on the contribution of higher multipoles in the Born approximation. Specifically, we progressively limit the number of contributing multipoles in the summation of equation (2), first considering only the lowest order term, then successively adding higher order terms. The summation starts at $\lambda = 2$ and increases in steps of $\Delta\lambda = 2$, due to parity conservation.

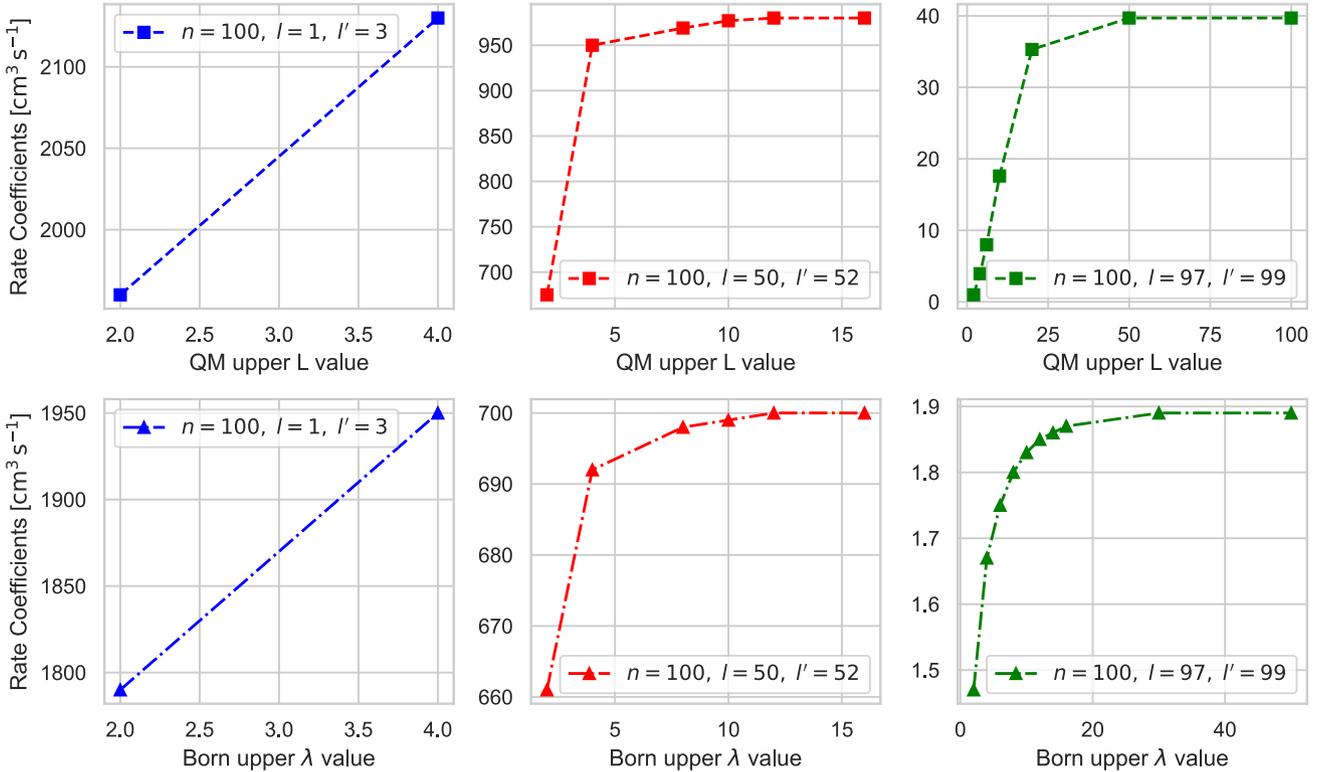
Fig. 2 clearly shows an increasing relative contribution from the higher pseudo-multipole terms to the TDSE QM L -sum compared to the Born multipole sum; for $l \gtrsim n/2$ the two summations disagree increasingly. It is evident that the first multipoles significantly influence and dominate the Born approximation's summation term, with the remaining multipoles contributing only 10 – 30 per cent. This raises the question of whether the disagreement between the Born and the TDSE QM approximations is only observed in quadrupole l -changing collisions and persists for higher multipole transitions. Comparison with TDSE QM approximation is essential for conclusive insights, especially given the BT Bethe approximation's internal agreement with the Born approximation. The agreement between the BT and the Born approximation would be worse if higher multipoles were restricted.

Referring to the Born summation term, equation (4), BT obtained the quadrupole collision strength without the contribution of higher multipoles. For higher l values, the multipoles physically contribute more to the sum as $l \rightarrow n$, compared to the first term of the sum. Considering the efficacy of the Born approximation in small l -changing collisions, any observed disagreement likely stems from the influence of higher multipoles on the summation term. We therefore suggest that the contribution of higher multipoles plays a pivotal role in the observed disagreement between the Born and the TDSE QM approximations, especially for large l -changing collisions. The quadrupole Born terms always dominate the total expression when summing over all multipoles without a limit. This completely differs from how the TDSE QM approximations vary based on its summation term. The Born approximation's multipole expansion involves distinct electric multipole interactions (e.g. dipole, quadrupole, octupole) integral to the electrostatic interaction governing the collision process.

We applied a limiting parameter to the TDSE QM approximation's summation term, equation (11), further investigating the origin of the discrepancy with the Born. The limiting parameter whose impact is illustrated in Fig. 2, is the only parameter that can restrict the contribution of higher multipoles on the expansion. We truncate the sum at that L value, beyond which the rate coefficient is constant with no further fluctuations. The Born and the TDSE QM behave in the same way inasmuch as they yield consistent results when higher multipoles are unrestricted.

Table 1. Representative TDSE QM, SCC, BTM, and Born rate coefficients [$\text{cm}^3 \text{s}^{-1}$] at $T = 100$ [K], for various n and l values. All of the higher (> 2) multipoles have been included in the Quantal Born and the TDSE results.

n	$l \rightarrow l'$	TDSE QM	SSC	BTM	Born
20	1 – 3	3.38×10^0	2.08×10^0	3.04×10^0	2.97×10^0
20	9 – 11	1.69×10^0	1.25×10^0	1.20×10^0	1.18×10^0
20	17 – 19	3.34×10^{-1}	3.18×10^{-1}	5.24×10^{-2}	5.52×10^{-2}
30	1 – 3	1.72×10^1	1.06×10^1	1.57×10^1	1.54×10^1
30	14 – 16	8.33×10^0	6.19×10^0	6.07×10^0	5.89×10^0
30	27 – 29	1.10×10^0	1.07×10^0	1.30×10^{-1}	1.34×10^{-1}
50	1 – 3	1.33×10^2	8.17×10^1	1.22×10^2	1.19×10^2
50	24 – 26	6.30×10^1	4.70×10^1	4.67×10^1	4.52×10^1
50	47 – 49	5.02×10^0	4.93×10^0	4.00×10^{-1}	4.10×10^{-1}
100	1 – 3	2.13×10^3	1.31×10^3	1.96×10^3	1.92×10^3
100	20 – 22	1.31×10^3	9.61×10^2	1.18×10^3	1.14×10^3
100	50 – 52	9.80×10^2	7.33×10^2	7.25×10^2	7.01×10^2
100	97 – 99	3.97×10^1	3.93×10^1	1.80×10^0	1.88×10^0
250	1 – 3	8.34×10^4	5.11×10^4	7.66×10^4	7.50×10^4
250	50 – 52	4.99×10^4	3.71×10^4	4.52×10^4	4.35×10^4
250	125 – 127	3.83×10^4	2.87×10^4	2.87×10^4	2.67×10^4
250	247 – 249	6.15×10^2	6.14×10^2	1.29×10^1	1.47×10^1
500	1 – 3	1.33×10^6	8.17×10^5	1.23×10^6	1.18×10^6
500	100 – 102	7.91×10^5	5.91×10^5	7.19×10^5	6.90×10^5
500	250 – 252	6.13×10^5	4.59×10^5	4.61×10^5	4.39×10^5
500	497 – 499	4.98×10^3	4.93×10^3	5.66×10^1	6.52×10^1


Figure 2. Variation of Born and TDSE QM rate coefficients [$\text{cm}^3 \text{s}^{-1}$] with the restriction of multipoles, at $T = 100$ [K].

We observed that the Bethe approximation, the first term in the Born summation (Burgess & Tully 2005), aligns well with the TDSE QM for small and intermediate l transitions, but deviates for large quadrupole l -changing collisions. We also noticed that when restricting the summation term to the first quadrupole multipole, the TDSE QM agrees approximately with the Born rate coefficient, including all

multipoles. This further agreement between the Born and the TDSE QM approximations supports that the primary source of disagreement between the latter for large l -changing collisions arises from the contribution of higher multipoles to their respective summation terms.

Table 2. Comparison table of dipole and quadrupole quantum mechanical (QM) rate coefficients [$\text{cm}^3 \text{s}^{-1}$] for transitions starting at the same l for the same n , at $T = 100$ [K] and $N_e = 1$ [cm^3].

n	$l \rightarrow l'$	Dipole	$l \rightarrow l'$	Quadrupole
10	1–2	1.08×10^1	1–3	2.04×10^{-1}
10	4–5	7.11×10^0	4–6	1.15×10^{-1}
10	7–8	3.39×10^0	7–9	4.54×10^{-2}
30	1–2	7.20×10^2	1–3	1.72×10^1
30	14–15	4.27×10^2	14–16	8.33×10^0
30	27–28	7.97×10^1	27–29	1.10×10^0
50	1–2	4.90×10^3	1–3	1.33×10^2
50	25–26	2.79×10^3	25–27	6.11×10^1
50	47–48	3.41×10^2	47–49	5.02×10^0
100	1–2	6.40×10^4	1–3	2.13×10^3
100	20–21	4.71×10^4	20–22	1.31×10^3
100	50–51	3.76×10^4	50–52	9.80×10^2
100	97–98	2.42×10^3	97–99	3.97×10^1
250	1–2	1.75×10^6	1–3	8.34×10^4
250	50–51	1.27×10^6	50–52	4.99×10^4
250	125–126	1.10×10^6	125–127	3.83×10^4
250	247–248	3.11×10^4	247–249	6.15×10^2
500	1–2	1.90×10^7	1–3	1.33×10^6
500	100–101	1.38×10^7	100–102	7.91×10^5
500	250–251	1.12×10^7	250–252	6.31×10^5
500	497–498	2.08×10^5	497–499	4.98×10^3

We find mathematical disagreement between the summation terms of the Born (4) and the TDSE QM (11) approximations when higher multipoles start to contribute. The Born summation follows a pattern based on $|l - l'|$ and extends up to $l + l'$ in an alternating sequence, while there is no corresponding physical interpretation of the TDSE QM sum.

5 TESTS ON THE RELEVANCE OF QUADRUPOLE RATES

Regardless of the discrepancies at high l , the fundamental question for astrophysical applications is whether quadrupolar rates affect the level populations of spectroscopically important states, and should be included in collisional-radiative models, alongside the dipolar rates.

To start with, we have compared the dipolar and quadrupolar rate coefficients for transitions starting at the same l for the same n . A range of values is shown in Table 2. It is clear that the quadrupolar rates are typically 14–100 times weaker than the dipolar ones.

Considering the limiting cases for both rates, we find that they depend similarly on n and the nuclear charge, Z_i . Hence, we expect that also for any other H-like atom or ion the quadrupole rates are negligible compared to the dipolar rates.

Still, one could wonder how much the inclusion of the quadrupolar rate changes the populations of all the states. To answer this question, the hydrogenic collisional radiative model, described in Hummer & Storey (1987) and based on Brocklehurst (1971), was modified to include the BTM rates, chosen as an upper limit for the low- l states which prove to be most affected.

Departure coefficients and line emissivities were compared with and without quadrupole transitions for $10^2 \leq T[\text{K}] \leq 10^6$, $10^2 \leq N_e[\text{cm}^{-3}] \leq 10^{12}$, and $2 \leq n \leq 100$ in Case A and Case B, depending on whether the Lyman lines were assumed optically thin or thick, respectively. The largest effects were found at the lowest temperatures and densities for Case A, where departure coefficients

Table 3. Table showing the maximum percentage change in emissivity due to the inclusion of quadrupole collision rates, at a selection of temperatures (K) and electron densities (cm^3), and the upper, n_u , and lower n_l , principal quantum numbers of the transition for which it occurs. All transitions with $n_u \leq 100$ were searched.

T (K)	Electron density (cm^3)	Transition $n_u - n_l$	Maximum percentage emissivity change
10^2	10^2	35–2	6.0
	10^4	19–2	4.8
	10^6	12–11	3.7
$10^{2.5}$	10^8	6–5	3.3
	10^{10}	5–4	2.3
	10^2	38–2	4.3
	10^4	20–2	3.7
	10^6	12–11	2.8
10^3	10^8	6–5	2.3
	10^{10}	4–3	0.88
	10^2	43–2	2.9
	10^4	22–2	2.6
	10^6	13–12	2.0
$10^{3.5}$	10^8	7–6	1.7
	10^{10}	4–3	0.66
	10^2	47–2	1.8
	10^4	23–2	1.7
	10^6	14–13	1.4
10^4	10^4	7–6	1.3
	10^{10}	4–3	0.51
	10^2	53–2	1.0
	10^4	28–2	0.93
	10^6	14–13	0.90
$10^{4.5}$	10^8	7–6	0.84
	10^{10}	4–3	0.35
	10^2	52–2	0.52
	10^4	29–2	0.47
	10^6	16–14	0.48
10^5	10^8	8–7	0.44
	10^{10}	5–4	0.21

changed by up to 8 per cent, while emissivities changed by 5 per cent. At typical nebular temperatures of 10^4 K no departure coefficients or emissivity was changed by more than 1 per cent. We note that a direct comparison of the quadrupole $l \rightarrow l + 2$ with the dipole $l \rightarrow l + 1$ rate coefficient does not capture all the physics, since the probability of population being transferred from a state nl to a state $nl + 2$ via the dipole $l \rightarrow l + 1 \rightarrow l + 2$ collisional process must also take into account the probability of a radiative decay from the $nl + 1$ state, which does not affect the quadrupole $l \rightarrow l + 2$ process.

In general, the impact of quadrupole transitions is expected to be greatest for those n above which radiative processes dominate the populations and below which populations are statistically distributed by rapid l -changing collisions. Thus the contribution of quadrupole rates is less significant at n values above and below this n regime, whose position is a function of the ambient electron density. For example Guzmán et al. (2019), state that the critical densities, at which radiative and collisional processes are in balance, are 30 cm^{-3} and 0.6 cm^{-3} , for $n = 30$ and $n = 50$, respectively. In Table 3 we show the transitions which exhibit the largest change when quadrupole transitions are added, as a function of electron temperature and density, for a range of conditions, including those typically found in photoionized nebulae.

6 CONCLUSIONS

We have developed a simple analytic formula (BTM) for quadrupole l -changing collisions which will be of interest to model astrophysical plasma emission, for example the hydrogen and helium-like recombination spectra (Guzmán et al. 2016; Badnell et al. 2021).

We find a good agreement between this BTM formula and results from our quantal Born calculations using the AUTOSTRUCTURE code, as well as between the SSC formula and the TDSE QM approximation.

We also find good agreement between our Born results and those we obtain from the TDSE method (Vrinceanu et al. 2012) for small- l ($\ll n$), but the two start to differ for intermediate- l ($\sim n/2$) and diverge increasingly for large- l ($\gtrsim n/2$).

The source of the disagreement between the two quantal results appears to lie with their representation of the higher (> 2) terms of the multipole expansion, which is much larger in the quadrupole case than the dipole one. There is a much larger relative contribution from the higher pseudo-multipole terms ($L = 2, 3, 4, \dots, n/2$) on the TDSE QM total, compared with the contribution of the higher multipoles ($\lambda = 2, 4, 6, \dots, l + l'$) to the Born one. Higher multipoles contribute significantly (approximately 90 percent) to the TDSE QM approximation, while applying limiting parameters on multipole expansion terms restricts their contribution and allows for a closer examination of rate coefficient variations. At this evaluation level, discrepancies between the TDSE and Born approximations highlight differences in how quadrupole l -changing collisions are treated. Given that TDSE is a full quantum approach, it is expected to provide a more rigorous description. However, further investigation is needed to fully understand the physical implications of these differences.

However, regardless of the reason for the discrepancy, it is clear that the quadrupolar rates are always going to be significantly lower than the dipolar ones, by typically two orders of magnitude. Their inclusion in a hydrogenic collisional radiative model for hydrogen shows minimal changes (a few percent) in the line emissivities, which we consider negligible for most astrophysical applications.

This is the last of a series of papers that began with Pengelly & Seaton (1964), advanced to the work of Vrinceanu & Flannery (2001), Vrinceanu et al. (2012, 2017), and Vrinceanu et al. (2019) leading to our studies Guzmán et al. (2016, 2017); Guzmán et al. (2019); Badnell et al. (2021).

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ACKNOWLEDGEMENTS

This paper is dedicated to the memory of Nigel Badnell. He contributed to large parts of this paper and worked for a long time on this topic. He received support from STFC (UK) through the University of Strathclyde APAP Network grant ST/R000743/1. ED worked on this topic with Nigel Badnell as an undergraduate student, and now acknowledges support from STFC (UK) via a PhD studentship. GDZ acknowledges support from STFC (UK) via the consolidated grants to the atomic astrophysics group at DAMTP, University of Cambridge (ST/P000665/1 and ST/T000481/1).

DATA AVAILABILITY

Results shown in the figures and tables will be shared on reasonable request to the corresponding author.

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APPENDIX A: BORN APPROXIMATION BY NRB

Consider a transition $q - q'$ between atomic states of hydrogen, where $q = nlm$, ignoring spin. Then,

$$Q(q \rightarrow q') = \frac{K_{q'}}{K_q} \int |F_{q'q}(\mathbf{K}_q, \mathbf{K}_{q'})|^2 d\Omega, \quad (\text{A1})$$

where \mathbf{K}_q is the initial momentum of the free electron. In the Born approximation the scattering amplitude is given by

$$F_{q'q}^B(\mathbf{K}_q, \mathbf{K}_{q'}) = \frac{1}{2\pi} \int \phi_{\mathbf{K}_{q'}}(\mathbf{r}_2) V_{q'q}(\mathbf{r}_2) \phi_{\mathbf{K}_q}(\mathbf{r}_2) d\mathbf{r}_2, \quad (\text{A2})$$

where $V_{q'q}$ is given by

$$V_{q'q}(\mathbf{r}_2) = \int \phi_{\mathbf{q}'}^*(\mathbf{r}_1) \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) \phi_{\mathbf{q}}(\mathbf{r}_1) d\mathbf{r}_1, \quad (\text{A3})$$

where

$$\phi_{\mathbf{K}_q}(\mathbf{r}) = e^{i\mathbf{K}_q \cdot \mathbf{r}}, \quad (\text{A4})$$

is a plane wave solution of

$$(\nabla^2 + K_q^2) \phi_{\mathbf{K}_q} = 0, \quad (\text{A5})$$

and $\phi_q(r)$ are atomic wavefunctions of the form

$$\phi_q(\mathbf{r}) = Y_{lm}(\hat{\mathbf{r}}) \frac{P_{nl}(r)}{r}, \quad (\text{A6})$$

where $Y_{lm}(\hat{\mathbf{r}})$ is a spherical harmonic and

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (\text{A7})$$

To see a formal (partial wave) solution with application to Coulomb Born, see Burgess, Hummer & Tully (1970), pp 226–230.

To proceed with the Born solution we do not need to make a partial wave analysis. Substituting equation (A3) into equation (A2), we obtain,

$$F_{q'q}^B(\mathbf{K}_q, \mathbf{K}_{q'}) = -\frac{1}{2\pi} \int \phi_{q'}^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) \times \int \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) e^{i\mathbf{K}\cdot\mathbf{r}_2} d\mathbf{r}_2 d\mathbf{r}_1, \quad (\text{A8})$$

where $\mathbf{K} = \mathbf{K}_q - \mathbf{K}_{q'}$ is the momentum transfer

A standard result in the literature comes from Bethe (1930) integral, given by

$$\int \frac{e^{i\mathbf{K}\cdot\mathbf{r}_2}}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_2 = \frac{4\pi}{K^2} e^{i\mathbf{K}\cdot\mathbf{r}_1} \quad \text{and} \quad \int \frac{e^{i\mathbf{K}\cdot\mathbf{r}_2}}{r_2} d\mathbf{r}_2 = \frac{4\pi}{K^2}. \quad (\text{A9})$$

Also, we always use orthonormal atomic wavefunctions

$$\int \phi_{q'}^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) d\mathbf{r}_1 = \delta_{qq'}. \quad (\text{A10})$$

Using equation (A9) and equation (A10) in equation (A8), we obtain,

$$F_{q'q}^B(\mathbf{K}) = -\frac{2}{K^2} \left[\int e^{i\mathbf{K}\cdot\mathbf{r}} \phi_{q'}^*(\mathbf{r}_1) \phi_q(\mathbf{r}_1) d\mathbf{r}_1 - \delta_{qq'} \right], \quad (\text{A11})$$

where

$$[\dots] = \langle q' | e^{i\mathbf{K}\cdot\mathbf{r}_1} - 1 | q \rangle. \quad (\text{A12})$$

We can re-write the solid angle as

$$d\Omega = d\phi \sin\theta d\theta. \quad (\text{A13})$$

Since we orientate K_q along the z-axis, then

$$K^2 = \mathbf{K} \cdot \mathbf{K} = (\mathbf{K}_{q'} - \mathbf{K}_q) \cdot (\mathbf{K}_{q'} - \mathbf{K}_q) = K_{q'}^2 + K_q^2 - 2K_q K_{q'} \cos\theta. \quad (\text{A14})$$

So,

$$2K dK = 2K_q K_{q'} \sin\theta d\theta \quad (\text{A15})$$

and

$$K_q K_{q'} \int \sin\theta d\theta = \int K dK. \quad (\text{A16})$$

Hence, using equation (A11) and equation (A16) into equation (A1), we obtain,

$$Q_{(q \rightarrow q')} = \frac{\pi}{K_q^2} \int \frac{d\phi}{2\pi} \int \frac{8dK}{K^3} |\langle q' | e^{i\mathbf{K}\cdot\mathbf{r}_1} - 1 | q \rangle|^2. \quad (\text{A17})$$

The collision strength $\Omega_{q'q}$ is defined from,

$$Q_{q'q} = Q(nlm \rightarrow n'l'm') = \frac{\pi}{K_q^2} \Omega_{q'q}. \quad (\text{A18})$$

In order to match results obtained by Burgess et al. (1997), expand the plane wave in spherical harmonics (Edmonds 1996), then

$$e^{i\mathbf{K}\cdot\mathbf{r}} = 4\pi \sum_{\lambda\mu} i^\lambda j_\lambda(Kr) Y_{\lambda\mu}^*(\hat{\mathbf{K}}) Y_{\lambda\mu}(\hat{\mathbf{r}}). \quad (\text{A19})$$

Then,

$$\Omega_{q'q} = 8 \int \frac{dK}{K^3} |E_{q'q}(K)|^2, \quad (\text{A20})$$

where

$$E_{q'q}(K) = 4\pi \sum_{\lambda\mu} i^\lambda Y_{\lambda\mu}^*(\hat{\mathbf{K}}) \langle q' | B_{\lambda\mu} | q \rangle \quad (\text{A21})$$

and

$$B_{\lambda\mu} = Y_{\lambda\mu}(\hat{\mathbf{r}}) (j_\lambda(Kr) - \delta_{\lambda 0}). \quad (\text{A22})$$

Then

$$|E_{q'q}(K)|^2 = 4\pi \sum_{\lambda\mu} |\langle q' | B_{\lambda\mu} | q \rangle|^2, \quad (\text{A23})$$

which still includes the magnetic quantum numbers m, m' .

The Wigner–Eckart theorem (Edmonds 1996) enables us to factor our the magnetic quantum numbers. Hence,

$$\begin{aligned} \langle n'l'm' | B_{\lambda\mu} | nlm \rangle &= (-1)^{l'-m'} \begin{pmatrix} l' & \lambda & l \\ -m' & \mu & m \end{pmatrix} \\ &\times \langle n'l' \| \mathbf{B}_\lambda \| nl \rangle \end{aligned} \quad (\text{A24})$$

and reduces the $B_{\lambda\mu}$ dependence to \mathbf{B}_λ , as μ is the 'magnetic' component of $Y_{\lambda\mu}$. Then the reduced matrix element is

$$\begin{aligned} \langle n'l' \| \mathbf{B}_\lambda \| nl \rangle &= (-1)^{l'} \left[\frac{(2l+1)(2\lambda+1)(2l'+1)}{4\pi} \right]^{1/2} \\ &\times \begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0 \end{pmatrix} \langle l' \| \mathbf{j}_\lambda \| l \rangle, \end{aligned} \quad (\text{A25})$$

where

$$\langle l' \| \mathbf{j}_\lambda \| l \rangle = \int_0^\infty dr P_{n'l'}(r) [j_\lambda(Kr) - \delta_{\lambda 0}] P_{nl}(r). \quad (\text{A26})$$

The Wigner 3-j symbol (Edmonds 1957, p.125) is given by,

$$\begin{aligned} \begin{pmatrix} l' & \lambda & l \\ 0 & 0 & 0 \end{pmatrix} &= (-1)^{L/2} \left[\frac{(l'+\lambda-l)(l'+l-\lambda)!}{(l'+\lambda+l+1)!} \right]^{1/2} \\ &\times \left[\frac{(L/2)!}{(L/2-l')!(L/2-\lambda)!(L/2-l)!} \right]^{1/2}, \end{aligned} \quad (\text{A27})$$

where $L = l' + \lambda + l$

The magnetic quantum numbers are then easily eliminated as in Burgess & Tully (2005), given also that,

$$\sum_{m'\mu m} \begin{pmatrix} l' & \lambda & l \\ m & \mu & m' \end{pmatrix}^2 = 1. \quad (\text{A28})$$

Which finally leaves us with equations (2) and (3) as presented in the paper.

APPENDIX B: BTM APPROXIMATION BY NRB

In this appendix we describe the modifications made to the Burgess & Tully (2005) approximation, which we now called BTM (Burgess and Tully Modified), especially for the analytic form of the quadrupole line strength of the target (S_2), given in equation (8) in the paper.

Looking at equation (17), equation (31) and equation (33) from the Burgess & Tully (2005) that present the collision strength, there had to be modifications to the quadrupole line strength of the target term, S_2 . Also, the rate coefficients are given in terms of energy, however zero excitation energy is assumed for quadrupole l -changing collisions.

Burgess & Tully (2005) present the collision strength in their equation (33) as,

$$\Omega_{ij} = \left(\frac{2}{15} \right) M^2 Z_p^2 S_2 \left(\frac{\alpha}{r_0} \right)^2, \quad (\text{B1})$$

where $\alpha^2 = 6$ agrees with equation (17) from the Burgess & Tully (2005) paper and r_0 can be determined by infinite energy or by $r_0 = \frac{c\alpha n^2}{Z_i}$

The quadrupole line strength for the target transition, S_2 is given by,

$$S_2(nl', nl' = l \pm 2) = (2)(2l+1)(2l'+1) \begin{pmatrix} l & 2 & l' \\ 0 & 0 & 0 \end{pmatrix} \times \left| \int P_{nl} r^2 P_{nl'} dr \right|^2, \quad (\text{B2})$$

where

$$(2)(2l+1)(2l'+1) \begin{pmatrix} l & 2 & l' \\ 0 & 0 & 0 \end{pmatrix}^2 = \frac{3l_>(l_>-1)}{(2l_>-1)} \quad (\text{B3})$$

and

$$\left| \int P_{nl} r^2 P_{nl'} dr \right|^2 = 100 \left(\frac{na_a}{2Z_t} \right)^2 (n^2 - l_>^2)^2 (n^2 - (l_>-1)^2). \quad (\text{B4})$$

Hence, we obtain the quadrupole line strength of the target term, S_2 , as we presented in equation (8) in the paper, which is,

$$S_2 = \left(\frac{300}{2} \right) \left(\frac{n}{2Z_t} \right)^4 \left(\frac{l_>(l_>-1)}{(2l_>-1)} \right) (n^2 - l_>^2)(n^2 - (l_>-1)^2). \quad (\text{B5})$$

Assuming that $l \gg 1$, and given that $l' = l \pm 2$ then equation (B5) simplifies to

$$S_2 = \frac{300}{2} \left(\frac{n}{2Z_t} \right)^4 l(n^2 - l^2)^2. \quad (\text{B6})$$

APPENDIX C: ANALYTIC EVALUATION

The analytic rate coefficient of BTM is given by substituting the collision strength, quadrupole line strength, and the effective size of the atom, as follows,

$$q_{nl \rightarrow nl'}^{BT} = \frac{2\sqrt{\pi M}}{\sqrt{kT(Ryd)}} \left(\frac{12}{15} \right) \left(\frac{Z_t}{c_0 n^2} \right)^2 \left(\frac{300}{2} \right) \left(\frac{n^4}{16Z_t^4} \right) \left(\frac{l_>(l_>-1)}{(2l_>-1)} \right) \times (n^2 - l_>^2)(n^2 - (l_>-1)^2) \times \frac{1}{(2l+1)\tau_0} a_0^3, \quad (\text{C1})$$

which is expressed in atomic units while the temperature (T) is expressed in Rydberg units. Burgess & Tully (2005) use

$$2\pi^{1/2} \left(\frac{a_0^3}{\tau_0} \right) = 2.17167 \times 10^{-8} \quad [\text{cm}^3 \text{s}^{-1}], \quad (\text{C2})$$

to convert atomic units to cgs units, which we follow as the SSC rate coefficient expression is given in cgs units. By making use of the appropriate values for constants, and for $T = 100$ K, we simplify equation (C1) as a numerical part, times an expression only written in terms of n and l , given by

$$q_{nl \rightarrow nl'}^{BT} = 4.90 \times 10^{-5} \times \left[\frac{1}{2l+1} \times \frac{l_>(l_>-1)}{2l_>-1} \times (n^2 - l_>^2)(n^2 - (l_>-1)^2) \right] \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C3})$$

We first consider approximate expressions for the case of intermediate l values, such that $1 \ll l \ll n$. For $l \gg 1$ we then have,

$$q_{nl \rightarrow nl'}^{BT} = 4.90 \times 10^{-5} \frac{l_>(n^2 - l_>^2)^2}{2(2l_>+1)} \quad [\text{cm}^3 \text{s}^{-1}], \quad (\text{C4})$$

which further simplifies to

$$q_{nl \rightarrow nl'}^{BT} = 1.23 \times 10^{-5} \times (n^2 - l^2)^2 \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C5})$$

Now, the full SSC simple rate coefficient, from Vrinceanu et al. (2012) is given by,

$$q_{nl \rightarrow nl'}^{SSC} = 1.294 \times 10^{-5} \sqrt{\frac{M}{m_e}} \frac{Z_p^2}{\sqrt{T}} \times \frac{n^2 [n^2(l+l') - l_<^2(l+l'+2|\Delta l|)]}{(l+1/2)|\Delta l|^3} \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C6})$$

Then, we can multiply equation (15) by a factor of $2/2$ so that the denominator can be easily aligned in a way that it matches the initial statistical weight of the BT rate coefficient of the form $1/(2l+1)$. We then obtain,

$$q_{nl \rightarrow nl'}^{SSC} = 3.9213 \times 10^{-5} \times \frac{n^2 [n^2(l_>-1) - (l_>-2)^2(l_>+1)]}{2(2l+1)} \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C7})$$

Then, similarly with the BTM evaluation, we can take the limit where $l \gg 1$ and simplify the SSC rate coefficient as,

$$q_{nl \rightarrow nl'}^{SSC} = 9.8 \times 10^{-6} \times n^2 [n^2 - l^2] \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C8})$$

If in addition $l \ll n$, then the expression further simplifies to determine the final results of the analytic comparison for intermediate l -changing transitions.

$$q_{nl \rightarrow nl'}^{SSC} = 9.8 \times 10^{-6} \times n^4 \quad [\text{cm}^3 \text{s}^{-1}] \quad (\text{C9})$$

and

$$q_{nl \rightarrow nl'}^{BT} = 1.23 \times 10^{-5} \times n^4 \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C10})$$

The SSC and the BTM expressions are finally compared for large l -changing transitions where the biggest disagreement is observed both numerically and analytically. The assumptions that hold for large l -changing transitions are slightly different from intermediate l -changing transitions. For large transitions, the SSC is in a highly accurate agreement with the TDSE QM. Additionally, numerical results show the highest level of agreement between the BTM and the Born. If we take $n = l_> + 1$, the initial SSC approximation, equation (15), for the large l -changing transitions is simplified into equation (C11).

$$q_{nl \rightarrow nl'}^{SSC} = 3.92 \times 10^{-5} \times \frac{2}{2} \times \frac{n^2 [2n^2(l_>-1) - 2(l_>-2)^2(l_>+1)]}{8(l_>+1/2)} \quad [\text{cm}^3 \text{s}^{-1}] \\ = 3.92 \times 10^{-5} \times \frac{1}{2} \times (l_>+1)^3 \times \frac{[(l_>^2-1) - (l_>-2)^2]}{(2l_>+1)} \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C11})$$

The same assumption holds for the BT rate coefficient expression evaluated on large l -changing transitions, so equation (C3) is further simplified into equation (C12).

$$q_{nl \rightarrow nl'}^{BT} = 4.90 \times 10^{-5} \times \frac{4l_>^2(2l_>+1)(l_>-1)}{(2l+1)(2l_>-1)} \quad [\text{cm}^3 \text{s}^{-1}]. \quad (\text{C12})$$

Also, for large l transitions, the assumption that $l \gg 1$ still holds therefore SSC and BT expressions are further simplified into equations (19) and (18), respectively, which are the final analytic results for the evaluation of large l transitions.

$$q_{nl \rightarrow n'l'}^{\text{SSC}} = 3.92 \times 10^{-5} \times l_{>}^3 \quad [\text{cm}^3 \text{s}^{-1}] \quad (\text{C13})$$

and

$$q_{nl \rightarrow n'l'}^{\text{BT}} = 9.80 \times 10^{-5} \times l_{>}^2 \times \quad [\text{cm}^3 \text{s}^{-1}] . \quad (\text{C14})$$

Therefore the final ratio of SSC/BT for large l transitions is approximately $0.4l_{>}$.

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