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A perturbative approach to the coupled outer-region equations for the electron-impact excitation of neutral atoms

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Abstract. We describe a perturbative approach to the solution of the coupled outer-region equations for the electron-impact excitation of neutral atoms, and which we have implemented within the computer code STGF. We compare the results from STGF for neutral Be and H with those that we have obtained with the non-perturbative R-matrix propagator code FARM. The excellent agreement obtained in general here points the way to the future extension of related codes for the calculation of energy levels and radiative rates in negative ions, photo-detachment cross sections and free–free electron transition data in the presence of a neutral atom.

1. Introduction

The R-matrix method is a very powerful approach for describing the dynamics of atoms and molecules. Configuration space is divided up into two regions: an inner one where the governing potentials are complicated to describe, often having no analytic form, and an outer one where the potentials have a rather simple form namely $r^{-\lambda-1}$ with $\lambda \geqslant 0$. This paper is concerned with the solution of the outer-region problem. We focus on electron collisions with atoms and ions and, in particular, excitation. For ions, there are two main approaches and associated computer codes. The FARM code solves the coupled outer-region equations without approximation using R-matrix propagator techniques (see Burke and Noble 1995), while the STGF code solves (initially) the uncoupled problem and treats the coupling potentials as a perturbation to the Coulomb potential (Seaton, unpublished, but see Berrington *et al* 1987). In our experience there is no significant difference to be found between the results of the two methods but we have found the perturbative approach (STGF) to be typically a factor of 3–5 faster computationally, in large cases, compared to the non-perturbative approach (FARM) as well as being more robust, in particular, when large pseudo-state expansions are being used. Furthermore, STGF does not exist in isolation. It is one of a suite of inter-related codes which can be used to calculate bound-state energies (STGB) and radiative rates (STGBB), photoionization and/or photorecombination cross sections (STGBF), free–free transition data (STGFF) and damping constants (STGD), in addition to excitation cross sections (STGF) (see Berrington *et al* 1987). To date, these codes require that the colliding electron impact upon a positively charged ion. In this paper we report on the development of STGF so that it can be applied to electron collisions with neutral atoms as well as ions, still treating the outer-region coupling potentials as a perturbation. This then points the way for the future development of the above suite of codes for application to neutral atoms, namely energies and radiative rates in negative ions, photo-detachment cross sections, etc.

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The outline of the paper is as follows. In section 2 we review the outer-region problem for neutral atoms. In section 3 we present results for the electron-impact excitation of neutral Be and H; in particular, we compare the results obtained from STGF with those that we have obtained from FARM. We finish with a short conclusion.

2. Theory

We assume that we have a solution to the scattering problem within some inner region $r \leqslant r_0$ and require to solve

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l_i(l_i+1)}{r^2} + \varepsilon_i\right) F_i(r) = \sum_{i'} V_{ii'}(r) F_{i'}(r) \tag{1}$$

in the outer region $r \geqslant r_0$ where the long-range multipoles $V_{ii'}$ are reduced to

$$V_{ii'}(r) = \sum_{\lambda} C^{\lambda}_{ii'}/r^{\lambda+1} \tag{2}$$

where $\lambda = 1, 2, 3 \ldots$. In the Coulomb case the multipole potentials are small perturbations to the Coulomb potential (Seaton 1985). For neutral atoms

$$|V_{ii'}(r)| \ll \left|\varepsilon - \frac{l_i(l_i+1)}{r^2}\right| \qquad \text{for} \quad r \geqslant r_0 \tag{3}$$

is often satisfied but it cannot be guaranteed for all values of ε, l and r; for example, $\varepsilon > 0$ such that

$$r = [l_i(l_i+1)/\varepsilon]^{1/2} \geqslant r_0. \tag{4}$$

However, effective-range theory for long-range potentials demonstrates that the Born approximation gives the correct expansion terms for the scattering phase shifts, as powers of the wavenumber k expanded about $k = 0$, up to (but not including) k^{2l+1} for $\lambda > 1$ (see O'Malley *et al* 1961, Levy and Keller 1963). Since equation (4) is satisfied only for $\varepsilon = k^2$ small, in general, this provides us with some justification to proceed in assuming that the long-range multipole potentials can still be treated as a perturbation in this instance as well.

2.1. Spherical Bessel functions

If the multipole potentials are neglected then the solutions of equation (1)† are simply related to spherical Bessel functions. We denote the regular ($\lambda = l + \frac{1}{2}$) and irregular ($\lambda = -l - \frac{1}{2}$) solutions of

$$\left(\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{\lambda^2 - \frac{1}{4}}{r^2} + \varepsilon\right) y_{\lambda}(r) = 0 \tag{5}$$

by s_l ($\equiv y_{l+1/2}$) and c_l ($\equiv y_{-l-1/2}$), by analogy with the Coulomb problem. They are related to the regular (j_l) and irregular (n_l) spherical Bessel functions via

$$s_l(r) = N r j_l(r) \qquad \text{and} \qquad c_l(r) = -N r n_l(r) \tag{6}$$

where N is a normalization constant.

The practical solution to the neutral atom problem cannot simply be obtained by setting the asymptotic Coulomb charge to zero ($z = 0$) everywhere in the solution to the Coulomb problem since the correct limiting behaviour as $z \to 0$ is not always obtained by such a procedure. So, we briefly review the differences from the solution to the Coulomb problem, which has been discussed by Seaton (1982, 1983, 1985).

† Sometimes known as Riccati–Bessel functions.

2.1.1. Positive energies. We set $\varepsilon = k^2$. We use s and c functions normalized to asymptotic forms given by

$$s_l(r) \underset{r\to\infty}{\sim} k^{-1/2}\sin(kr - l\pi/2) \qquad \text{and} \qquad c_l(r) \underset{r\to\infty}{\sim} k^{-1/2}\cos(kr - l\pi/2). \tag{7}$$

Then $W(c, s) = 1$, where W denotes the Wronskian. These are evaluated to first order (amplitude) or second order (phase) in the JWKB method using the expressions given by Burgess (1963) for neutral atoms. Solutions for $r \geqslant r_0$ are then obtained by inward integration using the Numerov method. For $\varepsilon > 0$, equation (5) has an (inner) point of inflection r_{I} given by

$$r_{\mathrm{I}} = [l(l+1)]^{1/2}/k. \tag{8}$$

When $r_{\mathrm{I}} > r_0$ the inward integration of s is unstable. A power-series solution to equation (5) at small r is given by

$$y_\lambda(r) = \sum_{n=0}^{\infty} a_n r^{n+\lambda+\frac{1}{2}} \tag{9}$$

where

$$a_n = -\varepsilon a_{n-2}[n(n+2\lambda)]^{-1} \tag{10}$$

with the normalization a_0 determined by the small-r behaviour, given by

$$s_l(r) \underset{r\to 0}{\sim} \frac{k^{l+1/2}}{(2l+1)!!} r^{l+1} \qquad \text{and} \qquad c_l(r) \underset{r\to 0}{\sim} \frac{(2l-1)!!}{k^{l+1/2}} r^{-l} \tag{11}$$

consistent with (7). When $r_{\mathrm{I}} > r_0$, c can, and should, still be evaluated by inward integration but there are problems where we do require, or prefer, a series solution for c; for example, in the absence of perturbations we can simply evaluate s and c at $r = r_0$ from equations (9)–(11).

2.1.2. Negative energies. Writing

$$\varepsilon = -1/\nu^2 \tag{12}$$

we see that the solution of equation (5) has no points of inflection. We look for exponentially decaying solutions θ with a power-series solution for large r given by

$$\theta = \mathrm{e}^{-r/\nu} \sum_{n=0}^{\infty} b_n r^{-n} \tag{13}$$

where, from (5),

$$b_n = \left(\frac{\nu}{2n}\right)[l(l+1) - n(n-1)]b_{n-1}. \tag{14}$$

The spatial derivative of θ (θ') is obtained trivially from (13). A complete perturbative solution for closed-channel long-range potentials (Seaton 1985) also requires $\dot\theta$ and $\dot\theta'$, where the dot denotes the energy derivative, with $W(\theta, \dot\theta)|_{r=r_0} = 1$ which obviates the need to determine b_0 explicitly. Explicit expressions for $\dot\theta$ and $\dot\theta'$ are given in an appendix to this paper. Again, θ and $\dot\theta$ can then be integrated inwards to $r = r_0$.

For completeness, we note that negative energy solutions for s and c can be obtained from section 2.1.1 on setting $k = \mathrm{i}/\nu$ and that they are complex for all values of ν and l.

2.2. Perturbation corrections

The first-order corrections to s, c and θ then follow as in the Coulomb case (see section 7.2 of Berrington *et al* 1987†). We note that the asymptotic contribution to the outer-region integrals can still be evaluated using the methods of Sil *et al* (1984) on, again, modifying the expressions for the amplitudes and phases in the complex plane according to Burgess (1963) for the neutral case.

3. Results

We have carried out LS-coupling 6CC ($2l2l', l, l' = 0, 1$) and 26CC (6CC plus $2l3l', l = 0, 1, l' = 0, 1, 2$) R-matrix calculations for the electron-impact excitation of neutral Be as well as 3CC (1s, 2s, 2p) and 6CC (3CC plus 3s, 3p, 3d) calculations for neutral H. Be was chosen as a typical neutral, with a relatively small R-matrix box, and H as the most extreme example for treating coupling as a perturbation. Consideration of box size is an important point. We wish to compare the perturbative results from STGF with the non-perturbative results from FARM. Both sets of calculations have the same solution for the inner region. The only difference arises from the treatment of the outer-region contribution. If we use a large configuration-interaction target expansion or, more importantly, a large pseudo-state expansion to allow for continuum coupling then this would result in a very large box size and severely limit the outer-region contribution. Since we wish to emphasize the outer-region contribution but still deal with a physically relevant problem (i.e. we do not want to set the inner-region contribution to zero) we use a small target expansion so as to consider the worst-case scenario. For this reason, the results that we present here should be viewed as relative rather than absolute. Finally, we note that all of our calculations involving the outer-region long-range multipole potentials included only the dipole and quadrupole terms since, for $\lambda \geqslant 3$, the treatment of STGF and FARM differs—STGF only includes a single multipole per transition, so the octupole potential is present in s $\rightarrow$ f transitions but not p $\rightarrow$ d, for example, while FARM includes both the dipole and octupole potentials in the latter case.

3.1. Be

In figure 1(*a*) we compare collision strengths for the $2s^2\,{}^1S \rightarrow 2p^2\,{}^3P$ transition in neutral Be that were obtained from 6CC calculations for the sum of the ${}^2P^o$ and ${}^2D$ symmetries, which dominate. We show results that were obtained both with and without the inclusion of outer-region long-range multipole potentials. In both cases, the results from STGF and FARM are indistinguishable and so we show a single curve for each. We see that the inclusion of outer-region multipole potentials has a significant effect for this transition. In figure 1(*b*) we show the difference between the collision strengths obtained from STGF and FARM when outer-region multipole potentials are included—it is typically $<0.1\%$. (When omitted, the difference is $<1 \times 10^{-5}$, except very close to threshold where it is a little larger.)

In figure 2 we show results for the same transition as in figure 1, but this time for the 26CC calculation. We see that the effect of the outer-region multipole potentials is severely reduced, since $r_0(6CC) = 17.2$, while $r_0(26CC) = 43.5$. The results from STGF and FARM are again indistinguishable in both cases, both with and without the inclusion of outer-region multipole potentials. We see, from figure 2(*b*), that the difference between the results from STGF and FARM is broadly reduced but it is slightly larger at the 'odd' energy (for three energies, the difference is only just off the scale). The former is to be expected because of

† There $W(c, s) = 1/\pi$.

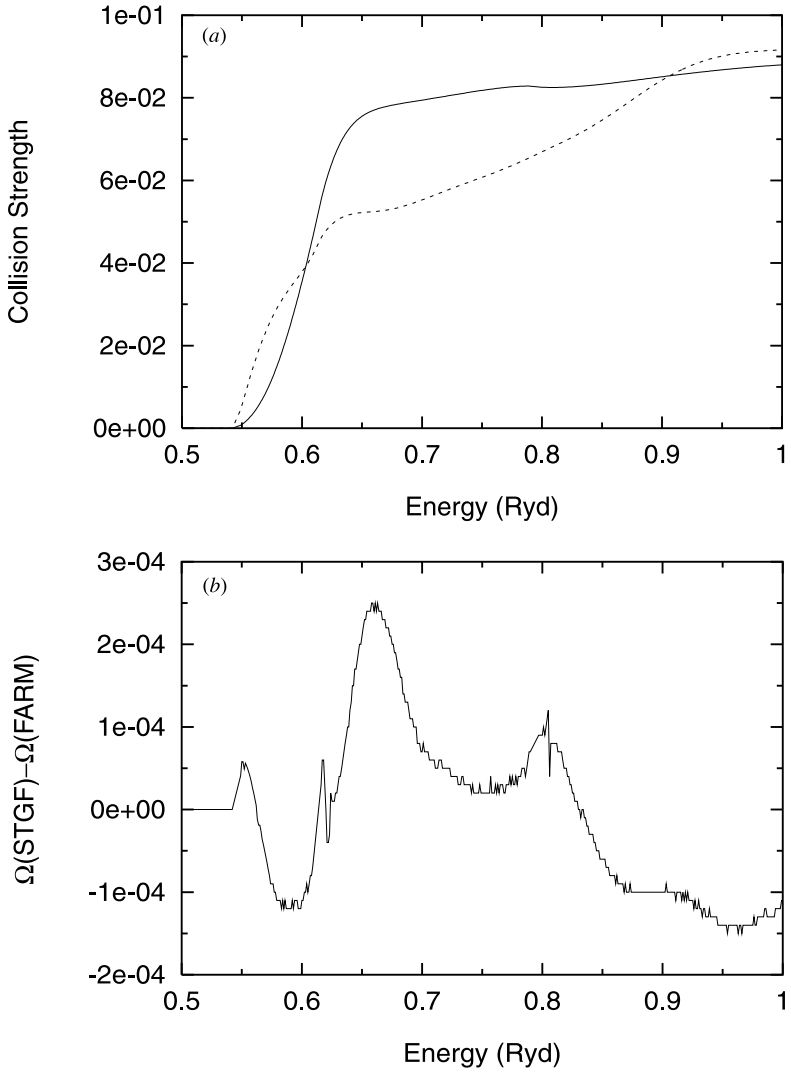

Figure 1. The $2s^2\,{}^1S \rightarrow 2p^2\,{}^3P$ transition in Be for the sum of the ${}^2P^o$ and ${}^2D$ symmetries from a 6CC *R*-matrix calculation. (*a*) Collision strength with (full curve) and without (broken curve) outer-region multipole potentials from STGF and FARM. (*b*) The difference between the collision strengths, with outer-region multipoles, calculated with STGF and FARM. All results are from this work.

the increased box size, while the latter is due to the large increase in the number of couplings, particularly to more highly excited states that are present in the 26CC calculation but not the 6CC. (This was verified by carrying out a 6CC calculation using r_0(26CC)—the difference fell to $\sim 10^{-5}$.) Furthermore, we have scanned through over 100 transitions in Be (for $2 \rightarrow 2$, $2 \rightarrow 3$ and $3 \rightarrow 3$ transitions) and noted only the tiniest of observable differences between the results from STGF and FARM. The effect of the outer-region multipoles is also severely reduced for these 26CC results, compared to the 6CC results, emphasizing the point about the role of the *R*-matrix box. Finally, we note that STGF is a little over (under) a factor of 5 faster than FARM for the 26CC calculation run with (without) the inclusion of outer-region

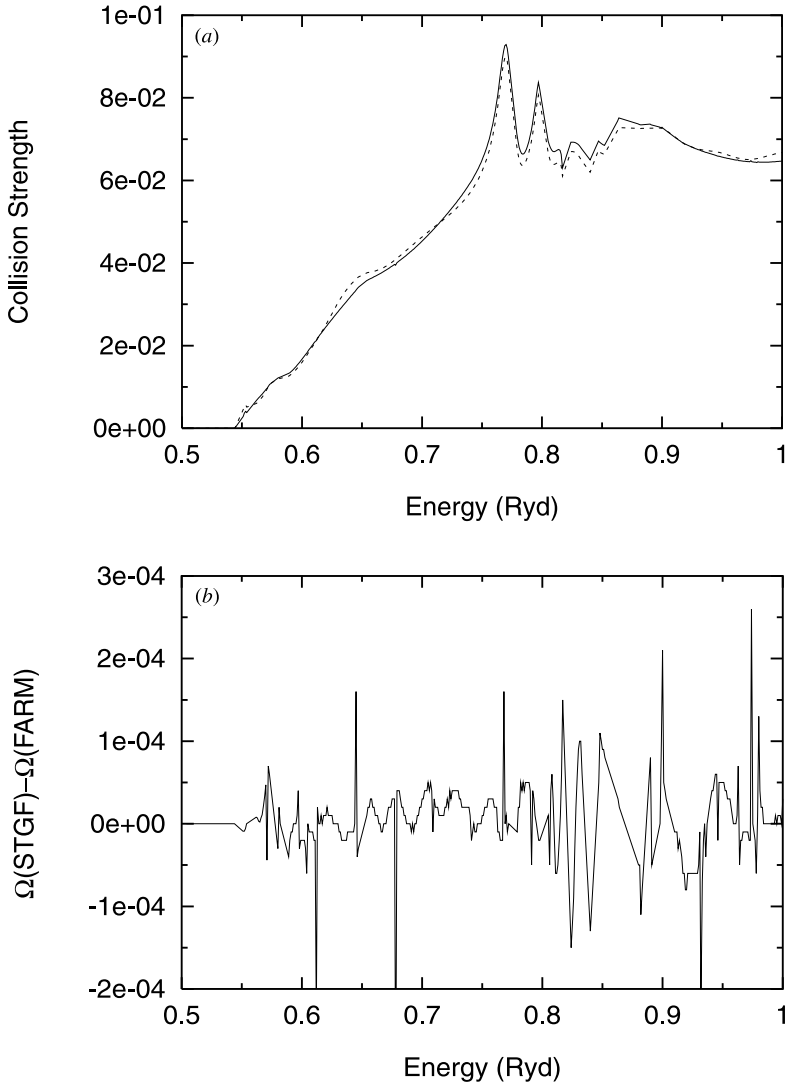

Figure 2. As figure 1, but from a 26CC *R*-matrix calculation. All results are from this work.

multipole potentials. (We took care to ensure that the exact same energy mesh was used in both sets of calculations—a linear one with $\Delta\varepsilon = 0.001$ Ryd, except that energies that occurred within 5×10^{-3} Ryd above a threshold were dropped as such energies are particularly time consuming to propagate.)

3.2. H

In figure 3 we compare collision strengths for the 1s $\rightarrow$ 2s transition in neutral H that were obtained from 3CC calculations summed over the $L = 0$–2 symmetries, which dominate. We find that only for collision energies within about 0.01 Ryd above the $n = 2$ threshold do the results from STGF and FARM start to differ appreciably. This is due to the presence of the outer-region potentials, as can be seen by comparison with the (single) curve for

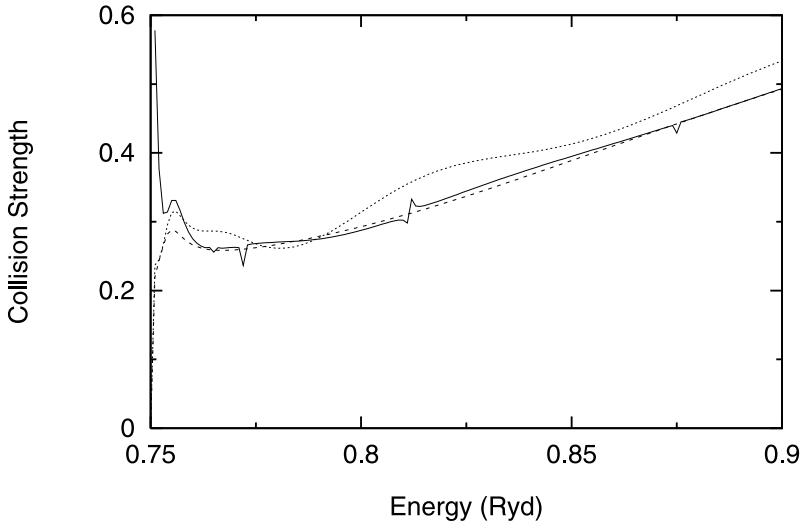

Figure 3. Collision strengths for the 1s $\rightarrow$ 2s transition in H from a 3CC R-matrix calculation for the sum of the $L = 0$–2 symmetries. Full curve, from STGF with outer-region multipole potentials; broken curve, from FARM with outer-region multipole potentials; dotted curve, without outer-region multipoles from STGF and FARM. All results are from this work.

the results obtained on omitting the outer-region multipole potentials. We find that going to a 6CC calculation significantly improves the situation since, $r_0(3\text{CC}) = 26.1$ while $r_0(6\text{CC}) = 47.3$. From equation (4) we see, for $r \approx r_0$, that the perturbations are relatively large for $\varepsilon \approx l(l+1)/r_0^2 \approx 0.01$ (3CC) and 0.003 (6CC) for $l = 2$, say†. Similar inaccuracies arise in the 6CC results just above the $n = 3$ threshold. These would be reduced by the inclusion of $n = 4$ states, and so on. Any realistic calculation necessitates the use of a large pseudo-state expansion and so the differences between the results from STGF and FARM can be expected to be of no practical significance. Furthermore, in practice, perturbations involving channels with ε small can be switched off, or the near-threshold energies can be skipped altogether. Finally, we note the presence of several small 'blips' in the perturbed STGF collision strength. There is no obvious explanation for them but they are peculiar to the degenerate coupling problem. We did not observe any such features in the case of Be.

4. Conclusion

We have described a perturbative approach for the treatment of the outer-region long-range multipole potentials that arise in the equations describing electron collisions with neutral atoms and, in particular, excitation. We have demonstrated the accuracy of such an approach by comparison with the results of the non-perturbative R-matrix propagator method. This points the way to the extension of related codes for application to (electrons plus) neutral atoms for the calculation of energies and radiative rates in negative ions, photo-detachment cross sections, etc.

† Off-diagonal dipole coupling between degenerate target states is equivalent to a modified r^{-2} diagonal potential, i.e. $\lambda = 1$ in equation (2), which is not covered by the effective-range theory discussed in section 2. If precise perturbative results are required here for H then they would be best obtained on diagonalizing the matrix of degenerate target-state dipole-coupling coefficients (Seaton 1961).

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Appendix

We consider the evaluation of θ, θ', $\dot{\theta}$ and $\dot{\theta}'$ in the neutral case. We switch to using p instead of θ, etc and follow the notation of Seaton (1985) who considered the Coulomb case. We rewrite our large-r power-series solution as

$$p = \mathrm{e}^{-r/\nu} \sum_{n=0}^{l} \beta_n x^{-n}/n! \tag{A1}$$

where $x = 2r/\nu$, then

$$\beta_n = (l+n)(l+1-n)\beta_{n-1} \tag{A2}$$

where we can take

$$\beta_0 = 1. \tag{A3}$$

Let

$$p = \phi S \tag{A4}$$

where

$$\phi = \mathrm{e}^{-r/\nu} \text{ etc.} \tag{A5}$$

Then, compare with the Coulomb case (Seaton 1985)

$$p' = \phi(aS + dT) \tag{A6}$$

$$\dot{p} = (\nu^3/2)\phi(bS + U) \tag{A7}$$

$$\dot{p}' = (\nu^3/2)\phi[(ab + c)S + bdT + aU + dV] \tag{A8}$$

where, now,

$$a = -1/\nu \tag{A9}$$

$$b = r/\nu^2 \tag{A10}$$

$$c = 1/\nu^2 \tag{A11}$$

and

$$d = -1/r. \tag{A12}$$

Furthermore,

$$T = \sum_{n=1}^{l} \beta_n x^{-n}/(n-1)! \tag{A13}$$

$$U = \sum_{n=1}^{l} \gamma_n x^{-n}/n! \tag{A14}$$

$$V = \sum_{n=1}^{l} \gamma_n x^{-n}/(n-1)! \tag{A15}$$

where, now,

$$\gamma_n = \beta_n n/\nu = \beta_n/\nu + (l+n)(l+1-n)\gamma_{n-1}$$
$$= (l+n)(l+1-n)[\beta_{n-1}/\nu + \gamma_{n-1}] \tag{A16}$$

and

$$\gamma_0 = 0. \tag{A17}$$

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