Eigenvectors and eigenvalues for the Keilson-Storer collision kernel

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The Keilson-Storer collision kernel has been used extensively to model how velocity-changing collisions affect spectral line shapes. None of the standard references use or refer to the eigenvectors or eigenvalues of the collision kernel. Here the eigenvectors and eigenvalues of the Keilson-Storer collision kernel are given for both one- and three-dimensional problems.

The Keilson-Storer[1] collision kernel has been used extensively to model how velocity-changing collisions affect spectral line shapes,[2,3] leading, in particular, to Dicke narrowing.[4] The same collision model has also been used for modeling spectroscopic phenomena involving velocity-selective optical pumping.[5] To solve the associated kinetic equation, iterations of the collision kernel have been used,[1] but, seemingly, no use of an eigenvector expansion has been considered. In spite of an extensive literature using the Keilson-Storer collision kernel, apparently its eigenvalues and eigenvectors are not known. It turns out that these are well-known simple functions. Elementary properties of the Keilson-Storer collision kernel are first reviewed to establish notation and the constraints on the parameters. Eigenfunctions and eigenvalues for the three-dimensional collision kernel are then presented together with an appropriate generating function. Next, the eigenvectors, eigenvalues, and a generating function for the corresponding one-dimensional kernel are given. Finally, to exemplify the use of the eigenvector-eigenvalue expansion, the time evolution of the three-dimensional velocity distribution is discussed, whose initial state is the delta function $\delta(\mathbf{v}-\mathbf{v}_0)$. The eigenvector representation of the time evolution of this state is formally very different from that obtained by Keilson and Storer using an iterative kernel method. It is shown that these two solutions are identical by making an appropriate expansion and then performing two summations.

Any linear kinetic equation describing purely velocity-changing collisions can be written in the form

$$\partial\rho(\mathbf{v})/\partial t=-\Gamma\rho(\mathbf{v})+\Gamma\int W(\mathbf{v}'\to\mathbf{v})\rho(\mathbf{v}')d\mathbf{v}' . \tag{1}$$

Here $\rho(\mathbf{v})$ is the velocity distribution which changes with time t due to collisions with molecules of a background (foreign) gas which is in thermal equilibrium. The loss rate $\Gamma\rho(\mathbf{v})$ is due to molecules changing from velocity $\mathbf{v}$ to some other velocity, while the integral sums the gain rates from velocity $\mathbf{v}'$ to velocity $\mathbf{v}$. In general Γ is also velocity dependent, but in the model of Keilson and Storer, Γ is taken as a constant. The integral kernel $W(\mathbf{v}'\to\mathbf{v})$ must satisfy the two conditions:

$$\text{(i)}\quad \int W(\mathbf{v}'\to\mathbf{v})d\mathbf{v}=1. \tag{2}$$

This is so that $\int\partial\rho/\partial t\, d\mathbf{v}=0$, i.e., molecules only change their velocities during collisions—they are neither created nor destroyed.

$$\text{(ii)}\quad \int W(\mathbf{v}'\to\mathbf{v})\rho_e(\mathbf{v}')d\mathbf{v}'=\rho_e(\mathbf{v}') , \tag{3}$$

so that at equilibrium, collisions change nothing. It is assumed that the appropriate equilibrium distribution is the classical Maxwellian

$$\rho_e(\mathbf{v})=(m/2\pi kT)^{3/2}\exp(-mv^2/2kT). \tag{4}$$

The collision kernel $W(\mathbf{v}'\to\mathbf{v})$ was modeled by Keilson and Storer as the Gaussian

$$W(\mathbf{v}'\to\mathbf{v})=\exp[-(\mathbf{v}-\alpha\mathbf{v}')^2/\sigma^2]/(\pi\sigma^2)^{3/2} . \tag{5}$$

This satisfies the normalization condition (i). The equilibrium condition (ii) necessitates that

$$\sigma^2=(1-\alpha^2)2kT/m . \tag{6}$$

This is easily proved, since the integral in Eq. (3) can be performed by "completing the square" of the quadratic in the exponent. One is left with a one-parameter family of collision kernels with the constraint that $|\alpha|<1$. That α represents the fractional transfer of average velocity follows from

$$\langle \mathbf{v}\rangle_{\text{after}}=\int\int \mathbf{v}W(\mathbf{v}'\to\mathbf{v})\rho(\mathbf{v}')d\mathbf{v}'d\mathbf{v} =\alpha\int \mathbf{v}'\rho(\mathbf{v}')dv'=\alpha\langle\mathbf{v}\rangle_{\text{before}} . \tag{7}$$

Two special cases of this collision kernel are (a) $\alpha=0$,

$$W(\mathbf{v}'\to\mathbf{v})=\rho_e(\mathbf{v}) , \tag{8}$$

which leads to the particularly simple kinetic equation with relaxation time Γ^{-1}.

$$\partial\rho/\partial t=\Gamma(\rho_e-\rho) . \tag{9}$$

Here it is assumed that $\int\rho\, dv=\int\rho_e d\mathbf{v}=1$. (b) $\alpha=1$,

$$W(\mathbf{v}'\to\mathbf{v})=\delta(\mathbf{v}'-\mathbf{v}) \tag{10}$$

and no relaxation occurs, i.e., $\partial\rho/\partial t=0$.

There are several considerations that can aid in looking for eigenvectors for any collision kernel. One of these is the requirement that $W(\mathbf{v}'\to\mathbf{v})$ is rotationally invariant. Thus a set of eigenvectors can be found in the form of being products of scalar functions of v^2 and spherical harmonics $Y_{lm}(\hat{\mathbf{v}})$ of the unit vector $\hat{\mathbf{v}}$. But more productive in the present case is to recognize that the integral of a product of two functions, each of which is the exponential of a quadratic, is again the exponential of a quadratic. Thus an exponential of a quadratic could be a generating function for the Keilson-Storer kernel. This is indeed the case. In fact, the generating function of Kumar,[6]

$$G(\mathbf{a},\gamma\mathbf{v})=\exp(-a^2+2\mathbf{a}\cdot\gamma\mathbf{v})=\frac{(\pi)^{1/2}}{2}\sum_{l,m,n}\frac{(-1)^n a^{2n+l}}{\Gamma(n+l+\frac{1}{2})}Y_{lm}^{*}(\hat{\mathbf{a}})(\gamma v)^l L_n^{l+1/2}(\gamma^2v^2)Y_{lm}(\hat{\mathbf{v}}) , \tag{11}$$

is close to being of this form. Here $L_n^{l+1/2}$ are the associated Laguerre polynomials normalized according to the Bateman series.[7] Multiplying this by the Gaussian $\exp(-\gamma^2v^2)$ does the job. It follows that

$$\int W(\mathbf{v}'\to\mathbf{v})\exp(-\gamma^2v'^2)G(\mathbf{a},\gamma\mathbf{v}')d\mathbf{v}'=\exp\left[\frac{-(\gamma^2v^2+\alpha^2a^2-2\alpha\mathbf{a}\cdot\gamma\mathbf{v})}{\alpha^2+\gamma^2\sigma^2}\right]=\exp(-\gamma^2v^2)G(\alpha\mathbf{a},\gamma\mathbf{v}) , \tag{12}$$

with the last equality valid if $\alpha^2+\gamma^2\sigma^2=1$. This latter condition is equivalent to $\gamma^2=m/2kT$.

On expanding the generating functions in Eq. (12) and equating coefficients of the functions of $\mathbf{a}$, it follows that

$$\int W(\mathbf{v}'\to\mathbf{v})\exp(-\gamma^2v'^2)(\gamma v')^l L_n^{l+1/2}(\gamma^2v'^2)Y_{lm}(\hat{\mathbf{v}}')d\mathbf{v}'=(\alpha)^{2n+l}\exp(-\gamma^2v^2)(\gamma v)^l L_n^{l+1/2}(\gamma^2v^2)Y_{lm}(\hat{\mathbf{v}}) . \tag{13}$$

Thus the eigenvalues of the Keilson-Storer kernel are the powers of α with the eigenfunctions being products of spherical harmonics and associated Laguerre polynomials weighted with the equilibrium Maxwellian and appropriate powers of γv. These are also the well-known eigenfunctions of the linearized Boltzmann equation for Maxwell molecules[8] and also the eigenfunctions for the three-dimensional harmonic oscillator.[6] For the latter problem in particular, there is a technical difference whether all of the exponential is contained in the eigenvector or whether the square root of the exponential is contained in the eigenvector. The advantage of this last modification is that the eigenvectors can be treated as elements of a Hilbert space (where there is a symmetry between vectors and linear functionals). As written, the collision kernel is not symmetric, so it does not produce a Hermitian operator, but it is easy to transform $W(\mathbf{v}'\to\mathbf{v})$ into a symmetric function (just multiply W by $\exp[\gamma^2(v'^2-v^2)/2]$) which is then the kernel for a Hermitian operator.

It is also noticed that the Keilson-Storer kernel does not cause changes in direction, each of the x, y, and z velocity components are independently affected. Equivalently, the Keilson-Storer kernel factors into one-dimensional kernels. Alternatively, if the velocity in only one direction is driven out of equilibrium by kinetic processes, then the other directions can be integrated over with a consequent simplification of the problem. The one dimensional kernel is

$$W_1(v'\to v)=\frac{\exp[-(v-\alpha v')^2/2u^2(1-\alpha^2)]}{[2\pi u^2(1-\alpha^2)]^{1/2}} . \tag{14}$$

Consistent with the fact that the eigenvectors of the three-dimensional kernel are the same as the eigenvectors of the three-dimensional harmonic oscillator, the eigenvectors of the one-dimensional kernel are the same as the eigenvectors of the one-dimensional harmonic oscillator, essentially Hermite polynomials times the appropriate Gaussian.

The generating function of the Hermite polynomials is[7]

$$G_1(a,\gamma v)=\exp(2a\gamma v-a^2)=\sum_n a^n/n!H_n(\gamma v) . \tag{15}$$

It follows that the integral of the collision kernel with this generating function has the form of being an exponential of a quadratic. This reduces to the simple relation

$$\int W_1(v'\to v)\exp(-\gamma^2v'^2)G_1(a,\gamma v')dv' =\exp(-\gamma^2v^2)G_1(\alpha a,\gamma v) , \tag{16}$$

provided γ is again chosen so that $\gamma^2=m/2kT$. Expansion of Eq. (16) in powers of a yields the eigenvector equation

$$\int W_1(v'\to v)\exp(-\gamma^2v'^2)H_n(\gamma v')dv' =\alpha^n\exp(-\gamma^2v^2)H_n(\gamma v) , \tag{17}$$

which shows that the eigenvalues of the one-dimensional Keilson-Storer kernel are the powers of α and the eigenvectors are essentially (up to the symmetry considerations mentioned previously) the one-dimensional harmonic oscillator wave functions.

The formal expansion of the three-dimensional velocity distribution in terms of the eigenvectors of the Keilson-Storer kernel is given by

$$\rho(\mathbf{v},t)=\sum_{l,m,n}\exp[-\Gamma(1-\alpha^{2n+l})t]a_{lmn} \times\exp(-\gamma^2v^2)(\gamma v)^l L_n^{l+1/2}(\gamma^2v^2)Y_{lm}(\hat{\mathbf{v}}) , \tag{18}$$

where the expansion coefficient a_{lmn} is determined by the velocity distribution at time zero according to the formula

$$a_{lmn}=\frac{2\gamma^3n!}{\Gamma(l+n+\frac{3}{2})}\int d\mathbf{v}(\gamma v)^l L_n^{l+1/2}(\gamma^2v^2) \times Y_{lm}^{*}(\hat{\mathbf{v}})\rho(\mathbf{v},0) . \tag{19}$$

For the special case that the initial distribution is the three-dimensional Dirac delta function $\delta(\mathbf{v}-\mathbf{v}_0)$, the expansion coefficient is given by

$$a_{lmn}=\frac{2\gamma^3 n!}{\Gamma(l+n+\frac{3}{2})}(\gamma v_0)^l L_n^{l+1/2}(\gamma^2 v_0^2)Y_{lm}^*(\hat{\mathbf{v}}_0) . \tag{20}$$

On substituting this evaluation of a_{lmn} into the eigenvector expansion, Eq. (18), it is found that the sum over m can be trivially performed to reduce the sum of spherical harmonics to a Legendre polynomial $P_l(\hat{\mathbf{v}}\cdot\hat{\mathbf{v}}_0)$. This gives the explicit result

$$\rho(\mathbf{v},t)=\frac{\gamma^3\exp(-\gamma^2v^2)}{2\pi}\sum_{l,n}\frac{(2l+1)n!}{\Gamma(l+n+\frac{3}{2})}\exp[-\Gamma(1-\alpha^{2n+l})t](\gamma^2 v_0 v)^l L_n^{l+1/2}(\gamma^2 v_0^2)L_n^{l+1/2}(\gamma^2 v^2)P_l(\hat{\mathbf{v}}_0\cdot\hat{\mathbf{v}}) . \tag{21}$$

Connection with the form of solution presented by Keilson and Storer[1] is obtained by expanding the exponential $\exp(\Gamma\alpha^{2n+l}t)$ in powers of t. The first term, the coefficient of t^0, is recognized as the eigenvector expansion of the initial state, the Dirac delta function $\delta(\mathbf{v}_0-\mathbf{v})$, so that the expanded form of the solution, Eq. (21), is

$$\rho(\mathbf{v},t)=\exp(-\Gamma t)\left[\delta(\mathbf{v}-\mathbf{v}_0)+\frac{\gamma^3\exp(-\gamma^2v^2)}{2\pi}\sum_{m=1}^{\infty}\frac{(\Gamma t)^m}{m!}\sum_{l,n}\frac{(2l+1)n!}{\Gamma(l+n+\frac{3}{2})}(\alpha^m)^{2n+l}\right.$$
$$\left.\times(\gamma^2 v_0 v)^l L_n^{l+1/2}(\gamma^2 v_0^2)L_n^{l+1/2}(\gamma^2 v^2)P_l(\hat{\mathbf{v}}_0\cdot\hat{\mathbf{v}})\right] . \tag{22}$$

The sums over n and l can now be formally accomplished. Using Eq. (20) of Sec. 10.12 of Ref. 7, the sum over the associated Laguerre functions gives a modified Bessel function and Eq. (22) becomes

$$\rho(\mathbf{v},t)=\exp(-\Gamma t)\left[\delta(\mathbf{v}-\mathbf{v}_0)+\frac{\gamma^3\exp(-\gamma^2v^2)}{2\pi(\gamma^2 v_0 v)^{1/2}}\sum_{m=1}^{\infty}\frac{(\Gamma t)^m}{m!\,\alpha^{m/2}(1-\alpha^{2m})}\exp\left[\frac{-\alpha^{2m}\gamma^2(v^2+v_0^2)}{1-\alpha^{2m}}\right]\right.$$
$$\left.\times\sum_l (2l+l)P_l(\hat{\mathbf{v}}_0\cdot\hat{\mathbf{v}})I_{l+1/2}\left[\frac{2\gamma^2 v_0 v\alpha^m}{1-\alpha^{2m}}\right]\right] . \tag{23}$$

The sum over l is performed using Eq. (1) of Sec. 7.15 of Ref. 7. After combining the exponential terms, the result can be written in the fairly simple form,

$$\rho(\mathbf{v},t)=\exp(-\Gamma t)\left[\delta(\mathbf{v}-\mathbf{v}_0)+\sum_{m=1}^{\infty}\frac{(\Gamma t)^m}{m!}\left[\frac{\gamma^2}{\pi(1-\alpha^{2m})}\right]^{3/2}\exp\left[\frac{2\gamma^2(\mathbf{v}-\alpha^m\mathbf{v}_0)^2}{1-\alpha^{2m}}\right]\right] , \tag{24}$$

which is the same as the result of Keilson and Storer except for notation. It is thus seen that the eigenfunction expansion, Eq. (21), is equivalent to the iterated kernel result of Keilson and Storer. However the form is different, the eigenfunction expansion showing the independent modes of decay of the velocity distribution according to the time evolution governed by the Boltzmann equation, while the iterated kernel solution expresses the answer in terms of a series of Gaussian distributions.

In conclusion, relaxation of the velocity distribution $\rho(\mathbf{v})$ is governed by the relaxation rates $\Gamma(1-\alpha^{2n+l})$, whether three dimensional or one dimensional. Γ can be interpreted as arising from the total cross section (for velocity changing collisions) and this is always reduced by a factor $(1-\alpha^{2n+l})$, which is, for α close to one, relatively small. The exception is for $2n+l$ very large, which is associated with very complicated velocity distributions. It follows that for most initial deviations from velocity equilibrium, the smallest relaxation rates and consequently the longest-lived deviations from equilibrium, will be associated with the smallest values of $2n+l$ and the simpler deviations from equilibrium. That is, at long times, only the simplest deviations from equilibrium will survive and these are governed by relaxation rates that are small compared to that associated with the total cross section.

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