THE QUANTUM MECHANICAL BOLTZMANN EQUATION

by

David K. Hoffman[+], John J. Mueller

and C. F. Curtiss

Theoretical Chemistry Institute, University of Wisconsin

Madison, Wisconsin 53715

ABSTRACT

A Boltzmann equation is derived from the N-particle Schroedinger equation. The development is based on the solution of the two particle quantum mechanical Liouville equation due to Green. The various approximations involved in the derivation are discussed and the collision integral and corrections are compared to their classical analogs. Further development of the collision integral yields the standard result, the usual Boltzmann collision integral in which the classical differential cross section is replaced by its quantum mechanical counterpart.

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+ Present Address: Department of Mathematical Physics, University of Adelaide, Adelaide, South Australia.

The quantum mechanical analog of the classical Boltzmann equation has been discussed by a number of authors.[1,2,3,4,5] The concept of a phase space in quantum mechanics is somewhat nebulous because of the Heisenberg uncertainty principle; but it has been well established that the proper correspondent to the classical distribution function is the Wigner distribution function.[4] In the classical limit (i.e. $\hbar \to 0$) this function obeys the classical equation and, in general, it possesses some, but not all, of the properties of a classical distribution (e.g. it is always real but not necessarily non-negative). In the Wigner representation both the position and momentum operators are simply multiplicative operators and, as a consequence, expressions for various statistical averages such as the stream velocity are of precisely the same form in the quantum mechanical treatment as in the classical treatment.

In this paper we derive an equation for the singlet distribution function which is a quantum mechanical analog of the Boltzmann equation. In the low density limit the equation is of the same form

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1. S. Chapman and T. G. Cowling, The Mathematical Theory of Non-uniform Gases (Cambridge University Press, London, 1960).
2. E. Wigner, Phys. Rev. 40, 749 (1932).
3. J. E. Moyal, Proc. Camb. Phil. Soc. 45, 99 (1949).
4. J. H. Irving and P. W. Zwanzig, J. Chem. Phys. 19, 1173 (1951).
5. R. F. Snider, J. Chem. Phys. 32, 1051 (1960).

as the classical equation except that the classical differential cross section is replaced by its quantum mechanical counterpart. The density correction terms are shown to be analogous to the correction terms to the classical equation due to Green.[6]

1. The Quantum Mechanical Liouville and B.B.G.K.Y. Equations

The state of an N-body quantum mechanical system is described by its density matrix, $\rho^{(N)}$. The time development of this function is described by the Schroedinger equation

$$i\hbar \frac{\partial \rho^{(N)}}{\partial t} = H^{(N)} \rho^{(N)} - \rho^{(N)} H^{(N)} \qquad 1$$

where $H^{(N)}$ is the N-particle Hamiltonian. The Wigner distribution function, $f^{(N)}$, is a Fourier transform of $\rho^{(N)}$ and is defined by the relation

$$f^{(N)}(\underline{x}^N, \underline{p}^N, t) = \left(\frac{2}{h}\right)^{3N} \int d\underline{x}'^N \exp\left(\frac{2i}{\hbar} \underline{p}^N \cdot \underline{x}'^N\right) \rho^{(N)}(\underline{x}^N - \underline{x}'^N, \underline{x}^N + \underline{x}'^N, t) \qquad 2$$

The superscript N denotes a vector in the N-particle space.

By transforming the Schroedinger equation into the Wigner representation one obtains a quantum mechanical analog of the Liouville equation. However, we do not wish to deal directly with this equation. Instead, following the procedure usual in the

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6. H. S. Green, Molecular Theory of Fluids, (North Holland Publishing Co., Amsterdam, 1952).

classical problem, we define lower order distribution functions, $f^{(g)}$, by the relations

$$f^{(g)} = \frac{1}{(N-g)!} \int d\underline{r}^{N-g} d\underline{p}^{N-g} f^{(N)} \qquad 1 \leq g < N \qquad (3)$$

A hierarchy of equations known as the quantum mechanical B.B.G.K.Y. equations governing the time evolution of the lower order distribution functions is obtained by integrating the quantum mechanical Liouville equation over the coordinates of some of the particles. If the total potential energy of the system is taken to be the sum of contributions associated with each pair of particles, the equation for any one distribution function involves only the function of next higher order. Hence, the whole hierarchy is interrelated and an exact solution for any one function cannot be obtained without, in effect, solving the original N-body Liouville equation. However, experience indicates that such detailed knowledge is not necessary for the description of the observed macroscopic behavior of the system. By making a suitable approximation, we terminate the hierarchy to obtain a closed set of equations which describe the phenomena of interest.

The equations for $f^{(1)}$ and $f^{(2)}$ which are obtained by integrating the quantum mechanical Liouville equation are[7]

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m} \cdot \frac{\partial}{\partial \underline{r}_1}\right\} f^{(1)} = \lambda \int d\underline{r}_2 \, d\underline{p}_2 \, \Theta^{(1,2)} f^{(2)} \qquad (4)$$

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7. H. S. Green, Proc. Phys. Soc. A; 66, 325 (1953).

and

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m}\cdot\frac{\partial}{\partial \underline{r}_1} + \frac{\underline{p}_2}{m}\cdot\frac{\partial}{\partial \underline{r}_2}\right\} f^{(2)} = \mathcal{O}^{(1,2)} f^{(2)} \tag{5}$$

$$+ \lambda \int d\underline{r}_3\, d\underline{p}_3 \left(\mathcal{O}^{(1,3)} + \mathcal{O}^{(2,3)}\right) f^{(3)}$$

where $\lambda = 1$, $\mathcal{O}^{(i,j)}$ is an integral operator defined by

$$\mathcal{O}^{(i,j)} = \frac{2}{h}\int d\underline{\sigma}\, \sin\left(\frac{\underline{\sigma}\cdot\underline{r}_{ij}}{h}\right)\left[\exp\frac{1}{2}\underline{\sigma}\cdot\left(\frac{\partial}{\partial \underline{p}_i} - \frac{\partial}{\partial \underline{p}_j}\right)\right]\chi(\underline{\sigma}) \tag{6}$$

and

$$\chi(\underline{\sigma}) = \frac{1}{h^3}\int d\underline{z}\, \varphi(z)\cos\left(\frac{\underline{\sigma}\cdot\underline{z}}{h}\right). \tag{7}$$

In the above equation the variable subscripts denote a particular particle. The quantity φ is the intermolecular potential and

$$\underline{r}_{ij} = \underline{r}_j - \underline{r}_i \tag{8}$$

The quantity λ multiplying the integrals in Eqs. 4 and 5 is an ordering parameter which is later set equal to one. The terms multiplied by λ represent the effect of collisions between the set of molecules described by the distribution function on the left and the rest of the molecules. When $\lambda = 0$ the equations

become quantum mechanical Liouville equations. We proceed by finding an approximate expression for $f^{(2)}$ as a functional of $f^{(1)}$ and use this result in Eq. 4 to obtain a closed equation for $f^{(1)}$.

If we expand the exponential

$$\exp\left[\frac{1}{2}\underline{\sigma}\cdot\left(\frac{\partial}{\partial \underline{p}_i}-\frac{\partial}{\partial \underline{p}_j}\right)\right]$$

which appears in the operator $\mathcal{O}^{(i,j)}$ in its power series we find the first non-zero contribution to the expansion arises from the term

$$\frac{1}{2}\underline{\sigma}\cdot\left(\frac{\partial}{\partial \underline{p}_i}-\frac{\partial}{\partial \underline{p}_j}\right) \qquad 9$$

This term gives rise to the classical operator

$$\mathcal{O}^{(i,j)}_{\text{classical}} = \frac{\partial\varphi(r_{ij})}{\partial \underline{r}_i}\cdot\frac{\partial}{\partial \underline{p}_i}+\frac{\partial\varphi(r_{ij})}{\partial \underline{r}_j}\cdot\frac{\partial}{\partial \underline{p}_j} \qquad 10$$

Higher terms in the expansion give rise to correction terms to the classical operator in powers of $\hbar^2$.

The operator $\mathcal{O}^{(i,j)}$ is zero for those values of the separation distance r_{ij} for which the potential and all its derivatives are effectively zero. This limits the integration over $\underline{r}_2$ in Eq. 4 to a sphere of a molecular diameter about $\underline{r}_1$.

2. Derivation of the Boltzmann Equation

The equation for $f^{(2)}$ can be simplified by assuming that only binary collisions are important. Since we are interested in a

solution of the $f^{(2)}$ equation for small values of n_{ij}, the integral on the right of Eq. 5 is negligible. That is, to develop the collision integral in Eq. 4 to order λ, we need $f^{(2)}$ to only zero order in λ. When this simplification is made we are left with the two particle quantum mechanical Liouville equation. Green[7] has given a solution of this equation as a functional of $f^{(1)}$,

$$f^{(2)} = \left(\frac{2}{h}\right)^6 \int d\underline{s}\, d\underline{r}_0\, d\underline{\sigma}\, d\underline{p}_0\, f^{(1)}(\underline{x}_0 - \tfrac{1}{2}\underline{r}_0, \tfrac{1}{2}\underline{P} - \underline{p}_0, t_0)$$

$$\times f^{(1)}(\underline{x}_0 + \tfrac{1}{2}\underline{r}_0, \tfrac{1}{2}\underline{P} + \underline{p}_0, t_0)\, \psi(\underline{r}+\underline{s}, \underline{p}_0+\underline{\sigma})\, \psi^*(\underline{r}-\underline{s}, \underline{p}_0-\underline{\sigma})$$

$$\times \exp\left\{-\frac{2i}{h}\left[\underline{p}\cdot\underline{s} + 2\,\underline{\sigma}\cdot\frac{\underline{p}_0}{m}(t-t_0) + \underline{\sigma}\cdot\underline{r}_0\right]\right\} \qquad 11$$

where

$$\underline{R} = \tfrac{1}{2}(\underline{r}_1 + \underline{r}_2) \qquad 12$$

$$\underline{P} = \underline{p}_1 + \underline{p}_2 \qquad 13$$

$$\underline{r} = \underline{r}_2 - \underline{r}_1 \qquad 14$$

$$\underline{p} = \frac{1}{2}(\underline{p}_2 - \underline{p}_1) \qquad 15$$

and

$$\underline{x}_0 = \underline{R} - \frac{1}{2}\frac{\underline{P}}{m}(t - t_0). \qquad 16$$

The wave function $\psi(\underline{r}, \underline{p}_0)$ appearing in this expression is a solution of the time independent Schroedinger equation

$$-\frac{\hbar^2}{m}\frac{\partial}{\partial \underline{r}} \cdot \frac{\partial}{\partial \underline{r}}\psi + \varphi(r)\psi = \frac{p_0^2}{m}\psi \qquad 17$$

with the boundary condition that it represents asymptotically an incident plane wave with momentum $\underline{p}_0$, and scattered waves. Green has shown that this expression for $f^{(2)}$ factors into a product of $f^{(1)}$'s in the precollision region of the phase space. This boundary condition corresponds to the "molecular chaos" condition which is assumed in the classical treatment.

Irreversibility enters the theory at this point. It arises, as in the classical theory, because we discriminate between the precollision ($\underline{p} \cdot \underline{r} < 0$ and r large) and postcollision ($\underline{p} \cdot \underline{r} > 0$ and r large) regions of the phase space by assuming that $f^{(2)}$ factors into a product of $f^{(1)}$'s in the precollision region. It can be shown that the solution given by Eq. 11 satisfies this condition, by a generalization of the argument used in the

derivation of Eq. 62. At very large separation distances, one can make use of the asymptotic form of ψ to show that in the precollision region $f^{(2)}$ depends only on the incident portion of ψ. A specialized form of this result is apparent in Eq. 61. When the exponential incident wave is used in Eq. 11 the integrations can be performed in a straightforward manner to yield the desired result. Since the classical and quantum mechanical two particle Liouville equations are identical outside the range of the potential, it follows that $f^{(2)}$ factors (as in the classical case) in the whole precollision portion of the phase space. That is, a point in this region of the phase space cannot describe in either the classical or quantum mechanical case two particles which have collided.

The $f^{(1)}$'s in Eq. 11, which are evaluated at time t_0, can be written in terms of $f^{(1)}$'s at time t by means of Eq. 4. To zero order in λ we obtain

$$f^{(1)}(\underline{x}_0 - \tfrac{1}{2}\underline{r}_0, \tfrac{1}{2}\underline{p} - \underline{p}_0, t_0) f^{(1)}(\underline{x}_0 + \tfrac{1}{2}\underline{r}_0, \tfrac{1}{2}\underline{p} + \underline{p}_0, t_0)$$

$$= f^{(1)}(\underline{x}_0 - \tfrac{1}{2}\underline{r}_0 + \tfrac{1}{m}(\tfrac{1}{2}\underline{p} - \underline{p}_0)(t - t_0), \tfrac{1}{2}\underline{p} - \underline{p}_0, t) \qquad (18)$$

$$\times f^{(1)}(\underline{x}_0 + \tfrac{1}{2}\underline{r}_0 + \tfrac{1}{m}(\tfrac{1}{2}\underline{p} + \underline{p}_0)(t - t_0), \tfrac{1}{2}\underline{p} + \underline{p}_0, t).$$

This result is consistent with the neglect of the three body collision terms which has been discussed previously. When this product is substituted into Eq. 11 the resulting expression for $f^{(2)}$ is independent of t_0. This can be seen by expanding the spatial

dependence of the $f^{(1)}$'s in a Taylor series about $\underline{R}$ and applying the technique illustrated in Eq. 30 to the various powers of

$$\underline{r}_0 + 2\frac{\underline{p}_0}{m}(t-t_0).$$

resulting from the expansion. An analogous property exists in the classical case.

If we combine Eqs. 4 and 5 and ignore three body terms, we have

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m}\cdot\frac{\partial}{\partial \underline{r}_1}\right\} f^{(1)}$$

$$= \int d\underline{r}_2 d\underline{p}_2 \left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m}\cdot\frac{\partial}{\partial \underline{r}_1} + \frac{\underline{p}_2}{m}\cdot\frac{\partial}{\partial \underline{r}_2}\right\} f^{(2)}. \qquad 19$$

To zero order in λ the operator in the integrand on the right commutes with the product of $f^{(1)}$'s and thus from Eqs. 11 and 18 we write

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m}\cdot\frac{\partial}{\partial \underline{r}_1}\right\} f^{(1)} = \left(\frac{2}{h}\right)^6 \int d\underline{r}_2 d\underline{p}_2 d\underline{s} d\underline{r}_0 d\underline{\sigma} d\underline{p}_0$$

$$\times f^{(1)}\left(\underline{r}_0 - \tfrac{1}{2}\underline{r}_0 + \tfrac{1}{m}\left(\tfrac{1}{2}\underline{P} - \underline{p}_0\right)(t-t_0), \tfrac{1}{2}\underline{P} - \underline{p}_0, t\right)$$

$$\times f^{(1)}\left(\underline{r}_0 + \tfrac{1}{2}\underline{r}_0 + \tfrac{1}{m}\left(\tfrac{1}{2}\underline{P} + \underline{p}_0\right)(t-t_0), \tfrac{1}{2}\underline{P} + \underline{p}_0, t\right)$$

$$\times \left\{\frac{\partial}{\partial t} + 2\frac{\underline{p}}{m}\cdot\frac{\partial}{\partial \underline{r}}\right\}\left\{\psi(\underline{r}+\underline{s}, \underline{p}_0+\underline{\sigma})\psi^*(\underline{r}-\underline{s}, \underline{p}_0-\underline{\sigma})\right.$$

$$\left.\times \exp -\frac{2i}{h}\left[\underline{p}\cdot\underline{s} + 2\underline{\sigma}\cdot\frac{\underline{p}_0}{m}(t-t_0) + \underline{\sigma}\cdot\underline{r}_0\right]\right\} \qquad 20$$

In obtaining this equation we have made use of the identity

$$\underline{p}_1 \cdot \left(\frac{\partial}{\partial \underline{r}_1}\right)_{\underline{r}_2} + \underline{p}_2 \cdot \left(\frac{\partial}{\partial \underline{r}_2}\right)_{\underline{r}_1} = \underline{p}_1 \cdot \left(\frac{\partial}{\partial \underline{r}_1}\right)_{\underline{r}} + 2\underline{p} \cdot \left(\frac{\partial}{\partial \underline{r}}\right)_{\underline{r}_1} \qquad 21$$

Now the integrand of the integral over $\underline{r}_2$ and $\underline{p}_2$ depends on two spatial coordinates which can be taken to be a gross position coordinate and a relative position coordinate. At equilibrium the system is spatially homogeneous and the functions are independent of the gross position coordinate. It is convenient to choose the gross position coordinate to be $\underline{r}_1$ and the relative coordinate to be $\underline{r}$. If we expand the spatial dependence of the product of $f^{(1)}$'s in Eq. 20 about $\underline{r}_1$, then the order of the gradient $\frac{\partial}{\partial \underline{r}_1}$ indicates the order of deviation from equilibrium. If we retain only terms through first order in this expansion we have

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m} \cdot \frac{\partial}{\partial \underline{r}_1}\right\} f^{(1)} = \int d\underline{r}_2 \, d\underline{p}_2 \left[2 \frac{\underline{p}}{m} \cdot \frac{\partial}{\partial \underline{r}} \bar{f}^{(2)} + \int d\underline{p}_0 \, \bar{f}_1^{(1)} \bar{f}_2^{(1)} \frac{\partial Q'}{\partial t} \right.$$

$$\left. + \frac{1}{2} \underline{r} \cdot \frac{\partial}{\partial \underline{r}_1} \int d\underline{p}_0 \, \bar{f}_1^{(1)} \bar{f}_2^{(1)} \frac{\partial Q'}{\partial t} + \underline{r} \, \frac{\underline{p}}{m} : \frac{\partial}{\partial \underline{r}} \frac{\partial}{\partial \underline{r}_1} \bar{f}^{(2)} \right.$$

$$\left. + \frac{\underline{p}}{m} \cdot \frac{\partial}{\partial \underline{r}} \int d\underline{r}_0 d\underline{p}_0 d\underline{\sigma} ds \left\{ \underline{r}_0 + 2 \frac{\underline{p}_0}{m} (t - t_0) \right\} \cdot \left\{ \bar{f}_1^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)} - \bar{f}_2^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)} \right\} Q \right.$$

$$+\frac{1}{2}\int d\underline{r}_0\, d\underline{p}_0\, d\underline{\sigma}\, d\underline{s}\left\{\underline{r}_0 + 2\,\frac{\underline{p}_0}{m}(t-t_0)\right\}\cdot\left\{\bar{f}_1^{(1)}\frac{\partial}{\partial \underline{r}_1}\bar{f}_2^{(1)} - \bar{f}_2^{(1)}\frac{\partial}{\partial \underline{r}_1}\bar{f}_1^{(1)}\right\}\frac{\partial Q}{\partial t}\Bigg] \qquad 22$$

where

$$\bar{f}_1^{(1)} = f^{(1)}\left(\underline{r}_1, \tfrac{1}{2}\underline{\rho} - \underline{p}_0, t\right) \qquad 23$$

$$\bar{f}_2^{(1)} = f^{(1)}\left(\underline{r}_1, \tfrac{1}{2}\underline{\rho} + \underline{p}_0, t\right) \qquad 24$$

$$Q = \left(\frac{2}{h}\right)^6 \Bigg[\psi\left(\underline{r}+\underline{s}, \underline{p}_0+\underline{\sigma}\right)\psi^*\left(\underline{r}-\underline{s}, \underline{p}_0-\underline{\sigma}\right)$$

$$\times \exp\left\{-\frac{2i}{h}\left[\underline{p}\cdot\underline{s} + 2\,\underline{\sigma}\cdot\frac{\underline{p}_0}{m}(t-t_0) + \underline{\sigma}\cdot\underline{r}_0\right]\right\}\Bigg] \qquad 25$$

$$Q' = \int d\underline{s}\, d\underline{r}_0\, d\underline{\sigma}\; Q \qquad 26$$

and

$$\bar{f}^{(2)} = \int d\underline{p}_0 \, \bar{f}_1^{(1)} \bar{f}_2^{(1)} Q' \qquad 27$$

In Eq. 26 we may make use of the fact that

$$\left(\frac{2}{h}\right)^3 \int d\underline{r}_0 \, e^{-2i(\underline{\sigma}-\underline{r}_0)/\hbar} = \delta(\underline{\sigma}) \qquad 28$$

to carry out the integrations over $\underline{r}_0$ and $\underline{\sigma}$ to obtain

$$Q' = \left(\frac{2}{h}\right)^3 \int d\underline{s} \, \psi(\underline{r}+\underline{s}, \underline{p}_0) \psi^*(\underline{r}-\underline{s}, \underline{p}_0) e^{-2i(\underline{p}\cdot\underline{s})/\hbar} \qquad 29$$

Thus Q' is independent of t, and the two terms in Eq. 22 which contain $\frac{\partial Q'}{\partial t}$ vanish. Upon comparing Eq. 29 with Eq. 2 we see that Q' is the steady state Wigner distribution function for a beam of particles with incident momenta $\underline{p}_0$ being scattered from a scattering center. In the next section we evaluate Q' at large distances from the scattering center.

The fifth term in the integrand of the integral in Eq. 22 can be simplified by the following integrations:

$$\int d\underline{s}\, d\underline{r}_0\, d\underline{\sigma} \left\{ \underline{r}_0 + 2\frac{\underline{p}_0}{m}(t-t_0) \right\} Q$$

$$= \left(\frac{2}{h}\right)^6 \int d\underline{s}\, d\underline{r}_0\, d\underline{\sigma}\, \psi(\underline{r}+\underline{s}, \underline{p}_0+\underline{\sigma})\, \psi^*(\underline{r}-\underline{s}, \underline{p}_0-\underline{\sigma})$$

$$\times \left(-\frac{\hbar}{2i}\right) \frac{\partial}{\partial \underline{\sigma}} \exp\left\{ -\frac{2i}{\hbar}\left[\underline{p}\cdot\underline{s} + \underline{\sigma}\cdot\underline{r}_0 + 2\,\underline{\sigma}\cdot\frac{\underline{p}_0}{m}(t-t_0) \right] \right\}$$

$$= \left(\frac{2}{h}\right)^3 \int d\underline{s}\, d\underline{\sigma}\, \psi(\underline{r}+\underline{s}, \underline{p}_0+\underline{\sigma})\, \psi^*(\underline{r}-\underline{s}, \underline{p}_0-\underline{\sigma})\, e^{-2i(\underline{p}\cdot\underline{s})/\hbar} \frac{\partial}{\partial \underline{\sigma}} \delta(\underline{\sigma}) \left(-\frac{\hbar}{2i}\right)$$

$$= \frac{\hbar}{2i}\left(\frac{2}{h}\right)^3 \int d\underline{s} \left[\psi^*(\underline{r}-\underline{s}, \underline{p}_0) \frac{\partial}{\partial \underline{p}_0} \psi(\underline{r}+\underline{s}, \underline{p}_0) \right.$$

$$\left. - \psi(\underline{r}+\underline{s}, \underline{p}_0) \frac{\partial}{\partial \underline{p}_0} \psi^*(\underline{r}-\underline{s}, \underline{p}_0) \right] e^{-2i(\underline{p}\cdot\underline{s})/\hbar}$$

Thus this expression, like Q', is independent of the time difference $t-t_0$.

The final term in Eq. 22 can be simplified by noting that

$$\frac{\partial Q}{\partial t} = -\frac{\partial Q}{\partial t_0} . \qquad 31$$

Thus

$$\frac{1}{2}\int d\underline{r}_0 d\underline{p}_0 d\underline{\sigma} d\underline{s} \left\{\underline{r}_0 + 2\frac{\underline{p}_0}{m}(t-t_0)\right\} \cdot \left\{\bar{f}_1^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)} - \bar{f}_2^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)}\right\} \frac{\partial Q}{\partial t}$$

$$= -\frac{1}{2}\frac{\partial}{\partial t_0}\int d\underline{r}_0 d\underline{p}_0 d\underline{\sigma} d\underline{s} \left\{\underline{r}_0 + 2\frac{\underline{p}_0}{m}(t-t_0)\right\} \cdot \left\{\bar{f}_1^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)} - \bar{f}_2^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)}\right\} Q$$

$$- \frac{1}{m}\int d\underline{p}_0 \; \underline{p}_0 \cdot \left\{\bar{f}_1^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)} - \bar{f}_2^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)}\right\} Q' .$$

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But the first term on the right in this expression vanishes because, as we have just shown, the expression given by Eq. 30 is independent of t_0. Thus Eq. 22 can be written

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}}{m}\cdot\frac{\partial}{\partial \underline{r}_1}\right\} f^{(1)} = \frac{1}{m}\int d\underline{r}_2\, d\underline{p}_2 \left[2\underline{p}\cdot\frac{\partial}{\partial \underline{r}} \bar{f}^{(2)} + \underline{r}\underline{p} : \frac{\partial}{\partial \underline{r}}\frac{\partial}{\partial \underline{r}_1} \bar{f}^{(2)} \right.$$

$$+ \underline{p}\cdot\frac{\partial}{\partial \underline{r}} \int d\underline{r}_0\, d\underline{p}_0\, d\underline{\sigma}\, d\underline{S} \left\{ \underline{r}_0 + 2\frac{\underline{p}_0}{m}(t-t_0) \right\} \cdot \left\{ \bar{f}_1^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)} - \bar{f}_2^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)} \right\} Q$$

$$\left. - \int d\underline{p}_0\, \underline{p}_0 \cdot \left\{ \bar{f}_1^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)} - \bar{f}_2^{(1)} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)} \right\} Q' \right] \qquad 33$$

It is shown in the next section that the first term on the right side of this equation gives rise to the quantum mechanical analog of the usual Boltzmann collision integral. It is shown in the following that the remaining terms[8], which are first order in the gradient $\frac{\partial}{\partial \underline{r}_1}$, correspond to the corrections to the classical collision integral due to Green.[6]

The correction terms to the classical Boltzmann

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8. The last two integrals in Eq. 33 are separately divergent and must be considered together to obtain a convergent result. They can easily be combined and written in terms of the operator $\mathcal{O}^{(1,2)}$ by essentially reversing the derivation given here. The form given here, however, has the advantage that it does not involve the complicated operator $\mathcal{O}^{(1,2)}$ explicitly.

collision integral can be written in the form[9]

$$\int d\underline{r}_2\, d\underline{p}_2\, \frac{\partial \psi}{\partial \underline{r}} \cdot \frac{\partial}{\partial \underline{p}} \left[\frac{1}{2} \underline{r} \cdot \frac{\partial}{\partial \underline{r}_1} \left(\bar{f}_1^{(1)\prime} \bar{f}_2^{(1)\prime} \right) + \frac{1}{2} \underline{r}' \cdot \left\{ \bar{f}_1^{(1)\prime} \frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)\prime} - \bar{f}_2^{(1)\prime} \frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)\prime} \right\} \right] . \tag{34}$$

The quantity $\underline{r}'$ is a position variable obtained as a function of $\underline{r}$ and $\underline{p}$ by first transforming $\underline{r}$ backward in time along the two particle collision trajectory until the two particles no longer interact and then transforming forward an equal length of time along a straight line trajectory (i.e. ignoring the effect of the potential). In writing the correction terms we have also used the definitions

$$\bar{f}_1^{(1)\prime} = f^{(1)}(\underline{r}_1, \underline{p}_1', t) \tag{35}$$

and

$$\bar{f}_2^{(1)\prime} = f^{(1)}(\underline{r}_1, \underline{p}_2', t) \tag{36}$$

where $\underline{p}_1'$ and $\underline{p}_2'$ are the initial values of $\underline{p}_1$ and $\underline{p}_2$ on the two particle trajectory.

In exact analogy to the quantum mechanical case which we have just discussed, the product $\bar{f}_1^{(1)\prime} \bar{f}_2^{(1)\prime}$ is a solution of the classical

two particle Liouville equation to zero order in the ordering parameter λ . Hence

$$\left\{\frac{\partial}{\partial t} + \frac{\underline{p}_1}{m}\cdot\frac{\partial}{\partial \underline{r}_1} + 2\,\frac{\underline{p}}{m}\cdot\frac{\partial}{\partial \underline{r}} - \frac{\partial \varphi}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{p}}\right\} \bar{f}_1^{(1)\prime}\,\bar{f}_2^{(1)\prime} = 0. \qquad 37$$

Using the identity[10]

$$\frac{\partial \varphi}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{p}} = \frac{2}{m}\left(\underline{p}\cdot\frac{\partial}{\partial \underline{r}} - \underline{p}'\cdot\frac{\partial}{\partial \underline{r}'}\right) \qquad 38$$

where $\underline{p}'$ is the initial relative momentum we find that to zero order in the gradient $\frac{\partial}{\partial \underline{r}_1}$ and the derivative with respect to the time

$$\underline{p}'\cdot\frac{\partial}{\partial \underline{r}'}\left[\bar{f}_1^{(1)\prime}\,\bar{f}_2^{(1)\prime}\right] = 0. \qquad 39$$

This result when substituted with Eq. 38 into Eq. 34 yields the following correction terms:

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10. A point in the phase space associated with the relative motion of the two particles may be described by $\underline{r}$ and $\underline{p}$ or alternately by $\underline{r}'$ and $\underline{p}'$. The total time derivative of an arbitrary function defined in this phase space (i.e. the derivative following a phase point) may be written in terms of either of the two coordinate systems

$$\frac{dF}{dt} = 2\,\frac{\underline{p}}{m}\cdot\frac{\partial F}{\partial \underline{r}} - \frac{\partial \varphi}{\partial \underline{r}}\cdot\frac{\partial F}{\partial \underline{p}} = 2\,\frac{\underline{p}'}{m}\cdot\frac{\partial F}{\partial \underline{r}'}.$$

Thus Eq. 38 follows. [See D. K. Hoffman and C. F. Curtiss, Phys. of Fluids 9, 1887 (1964)]

$$\frac{1}{m}\int d\underline{r}_2\, d\underline{p}_2 \Big[\underline{r}\,\underline{p} : \frac{\partial}{\partial \underline{r}}\frac{\partial}{\partial \underline{r}_1}\left(\bar{f}_1^{(1)\prime}\bar{f}_2^{(1)\prime}\right) + \underline{p}\cdot\frac{\partial}{\partial \underline{r}}\left(\underline{r}'\cdot\left\{\bar{f}_1^{(1)\prime}\frac{\partial}{\partial \underline{r}_1}\bar{f}_2^{(1)\prime} - \bar{f}_2^{(1)\prime}\frac{\partial}{\partial \underline{r}_1}\bar{f}_1^{(1)\prime}\right\}\right) - \underline{p}'\cdot\left\{\bar{f}_1^{(1)\prime}\frac{\partial}{\partial \underline{r}_1}\bar{f}_2^{(1)\prime} - \bar{f}_2^{(1)\prime}\frac{\partial}{\partial \underline{r}_1}\bar{f}_1^{(1)\prime}\right\}\Big] \qquad 40$$

In this form the classical correction terms are analogous to the quantum mechanical correction terms given by Eq. 33.

In the classical limit

$$\int d\underline{\sigma}\, d\underline{s}\, Q \longrightarrow \delta\left(\underline{r}_0 + 2\,\frac{\underline{p}_0}{m}(t-t_0) - \underline{r}'\right)\delta(\underline{p}_0 - \underline{p}') \qquad 41$$

If this substitution is made in Eq. 33 then Eq. 40 is obtained. The difference between the classical and quantum mechanical forms lies in the fact that there is no well defined quantum mechanical trajectory and hence the quantities $\underline{r}'$ and $\underline{p}'$ are replaced by averages in the quantum mechanical treatment.

3. <u>The Zero Order Collision Integral</u>

We next consider the primary term on the right of Eq. 33

$$\frac{2}{m}\int d\underline{r}_2 d\underline{p}_2\, \underline{p}\cdot\frac{\partial}{\partial \underline{r}}\,\bar{f}^{(2)} = \frac{16}{m}\int d\underline{r}\, d\underline{p}\, \underline{p}\cdot\frac{\partial}{\partial \underline{r}}\,\bar{f}^{(2)} \qquad 42$$

As has been mentioned, this term, which is of zero order in the gradient $\frac{\partial}{\partial \underline{r}_1}$, gives rise to the quantum mechanical analog of the usual Boltzmann collision integral. By Gauss' theorem one has

$$\frac{16}{m}\int d\underline{r}\, d\underline{p}\, \underline{p}\cdot\frac{\partial}{\partial \underline{r}}\,\bar{f}^{(2)} = \frac{16}{m}\lim_{D\to\infty} D^2 \int d\hat{\underline{k}}\, d\underline{p}\, (\hat{\underline{k}}\cdot\underline{p})\,\bar{f}^{(2)} \qquad 43$$

The function $\bar{f}^{(2)}$ in the surface integral is evaluated at $\underline{r} = D\hat{\underline{k}}$.

Let us examine the integral Q' defined by Eq. 29. One sees from Eq. 43 that it is necessary to evaluate Q' only for large values of r. We write $\psi(\underline{r},\underline{p}_0)$ in terms of an incident plane wave and a scattered wave $\psi_s(\underline{r},\underline{p}_0)$ as follows

$$\psi(\underline{r},\underline{p}_0) = e^{i(\underline{p}_0\cdot\underline{r})/\hbar} + \psi_s(\underline{r},\underline{p}_0) \qquad 44$$

For large values of r we make use of a translation theorem to show that

$$\psi_s(\underline{r}+\underline{s},\underline{p}_0) \longrightarrow e^{i p_0(\hat{\underline{k}}\cdot\underline{s})/\hbar}\,\psi_s(\underline{r},\underline{p}_0). \qquad 45$$

To prove this theorem one writes $\psi_s(\underline{r}+\underline{s},\underline{p}_0)$ in a Taylor series expansion

$$\psi_s(\underline{r}+\underline{s}, \underline{p}_0) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(\underline{s}\cdot\frac{\partial}{\partial \underline{r}}\right)^n \psi_s(\underline{r}, \underline{p}_0) \qquad 46$$

Now for large r

$$\psi_s(\underline{r}, \underline{p}_0) \longrightarrow \frac{1}{r} e^{i(p_0 r)/\hbar} f(\vartheta_0) \qquad 47$$

where $f(\vartheta_0)$ is the angular amplitude of the scattered wave and $\cos\vartheta_0 = \hat{p}_0 \cdot \hat{k}$. If one substitutes Eq. 47 into Eq. 46 and keeps only terms of order $\frac{1}{r}$ one finds that

$$\psi_s(\underline{r}+\underline{s}, \underline{p}_0) = \sum_{n=0}^{\infty} \frac{1}{n!}\left[\frac{i}{\hbar} p_0 (\hat{k}\cdot\underline{s})\right]^n \psi_s(\underline{r}, \underline{p}_0) + O\left(\frac{1}{r^2}\right)$$

$$= e^{i p_0 (\hat{k}\cdot\underline{s})/\hbar} \psi_s(\underline{r}, \underline{p}_0) + O\left(\frac{1}{r^2}\right). \qquad 48$$

This establishes the theorem.

From Eq. 29, 44, and 45 it follows that

$$Q' \longrightarrow \left(\frac{2}{h}\right)^3 \int d\underline{s} \Big[e^{2i\,\underline{s}\cdot(p_0 - p)/\hbar}$$

$$+ e^{i\,\underline{s}\cdot(p_0 + p_0\hat{\underline{k}} - 2p)/\hbar}\; e^{i\,D(p_0\cdot\hat{k})/\hbar}\, \psi_s^*(D\hat{\underline{k}}, p_0)$$

$$+ e^{i\,\underline{s}\cdot(p_0 + p_0\hat{\underline{k}} - 2p)/\hbar}\; e^{-i\,D(p_0\cdot\hat{\underline{k}})/\hbar}\, \psi_s(D\hat{\underline{k}}, p_0)$$

$$+ e^{2i\,\underline{s}\cdot(p_0\hat{\underline{k}} - p)/\hbar}\, \psi_s(D\hat{\underline{k}}, p_0)\, \psi_s^*(D\hat{\underline{k}}, p_0) \Big] .$$

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which can be reduced by integration over $\underline{S}$ to

$$Q' \longrightarrow \Big[\delta(p_0 - p) + \delta(p - p_0\hat{\underline{k}})\, \psi_s(D\hat{\underline{k}}, p_0)\, \psi_s^*(D\hat{\underline{k}}, p_0)$$

$$+ 2\,\delta\left(p - \tfrac{1}{2}p_0 - \tfrac{1}{2}p_0\hat{\underline{k}}\right) \mathrm{Re}\left\{ e^{-i\,D(p_0\cdot\hat{\underline{k}})/\hbar}\, \psi_s(D\hat{\underline{k}}, p_0) \right\} \Big]$$

50

The differential cross section $\sigma(\vartheta_0)$ is

$$\sigma(\vartheta_0) = D^2 \psi_s(D\hat{K}, p_0)\, \psi_s^*(D\hat{K}, p_0) \qquad 51$$

Hence

$$Q' \rightarrow \Big[\delta(p_0 - p) + \delta(p - p_0\hat{K})\frac{1}{D^2}\sigma(\vartheta_0) + 2\,\delta(p - \tfrac{1}{2}p_0 - \tfrac{1}{2}p_0\hat{K})\,\mathrm{Re}\left\{ e^{-iD(p_0\cdot\hat{K})/\hbar}\,\psi_s(D\hat{K}, p_0)\right\}\Big] \qquad 52$$

To complete the evaluation of Q' we examine the final term in this expression. For large values of D,

$$e^{-iD(p_0\cdot\hat{K})/\hbar} \rightarrow \frac{\hbar}{p_0 D}\Big[\sum_{\substack{\ell = \\ 0,2,4,\ldots}} (2\ell+1)\sin\left(\frac{p_0 D}{\hbar}\right) P_\ell(\cos\vartheta_0) + i \sum_{\substack{\ell = \\ 1,3,5,\ldots}} (2\ell+1)\cos\left(\frac{p_0 D}{\hbar}\right) P_\ell(\cos\vartheta_0)\Big] \qquad 53$$

Since

$$\sum_{\substack{\ell = \\ 0,2,4,\ldots}} (2\ell+1) P_\ell(\cos\vartheta_0) = \delta(\cos\vartheta_0 - 1) + \delta(\cos\vartheta_0 + 1) \qquad 54$$

and

$$\sum_{\substack{\ell = \\ 1,3,5,\ldots}} (2\ell+1)\, P_\ell(\cos\vartheta_o) = \delta(\cos\vartheta_o - 1) - \delta(\cos\vartheta_o + 1) \qquad 55$$

the exponential can be written

$$e^{-i D(p_o \cdot \hat{\underline{k}})/\hbar} \longrightarrow \frac{\hbar}{p_o D}\left[\sin\left(\frac{p_o D}{\hbar}\right)\left\{\delta(\cos\vartheta_o - 1) + \delta(\cos\vartheta_o + 1)\right\}\right.$$

$$\left. + i\cos\left(\frac{p_o D}{\hbar}\right)\left\{\delta(\cos\vartheta_o - 1) - \delta(\cos\vartheta_o + 1)\right\}\right] \qquad 56$$

If one combines Eqs. 47 and 56 one then finds that

$$2\,\mathrm{Re}\left[e^{-i D(p_o \cdot \hat{\underline{k}})/\hbar}\, \psi_s(D\hat{\underline{k}}, p_o)\right] \longrightarrow$$

$$2\,\mathrm{Re}\left[\frac{\hbar f(\vartheta_o)}{p_o D^2}\left\{\sin\left(\frac{2p_o D}{\hbar}\right) - i\cos\left(\frac{2p_o D}{\hbar}\right)\right\}\delta(\cos\vartheta_o + 1) + i\,\delta(\cos\vartheta_o - 1)\right] \qquad 57$$

Since D is large, $\sin\left(\frac{2p_o D}{\hbar}\right)$ and $\cos\left(\frac{2p_o D}{\hbar}\right)$ are rapidly oscillating functions[11] and are effectively zero on integration over p_o.

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11. Since this expression has a pole at $p_o = 0$, special consideration must be given to the integration over this point. From Eq. 52 we see that $p_o = 0$ implies that $p = 0$ and hence the extra factor of p in the integrand of the integral in Eq. 43 implies that this pole does not contribute to the integral.

Hence in the above equation we neglect terms proportional to $\sin\left(\frac{2p_0 D}{\hbar}\right)$ and $\cos\left(\frac{2p_0 D}{\hbar}\right)$ to obtain

$$2\,Re\left[e^{-iD(p_0\cdot\hat{K})/\hbar}\,\psi_S(D\hat{K},p_0)\right]\longrightarrow$$

$$-\frac{2\hbar}{p_0 D^2}\,Im\{f(0)\}\,\delta(\cos\vartheta_0-1). \qquad (p_0\neq 0.) \tag{58}$$

The optical theorem states that

$$Im\{f(0)\}=\frac{p_0}{4\pi\hbar}\,\Sigma \tag{59}$$

where Σ is the total cross section. Thus we write[12]

$$2\,Re\left[e^{-iD(p_0\cdot\hat{K})/\hbar}\,\psi_S(D\hat{K},p_0)\right]\longrightarrow \tag{60}$$

$$-\frac{1}{D^2}\,\Sigma\,\delta(\hat{p}_0-\hat{K}) \qquad (p_0\neq 0)$$

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12. If $g(\hat{K})$ is any well behaved function of the unit vector $\hat{K}$

$$\int d\hat{K}\,\delta(\cos\vartheta_0-1)\,g(\hat{K})=\int d\varphi_0\,d(\cos\vartheta_0)\,\delta(\cos\vartheta_0-1)$$

$$\times g(\sin\vartheta_0\cos\varphi_0,\sin\vartheta_0\sin\varphi_0,\cos\vartheta_0)=\int d\varphi_0\,g(\hat{p}_0)=2\pi g(\hat{p}_0)$$

Thus the identity

$$\delta(\cos\vartheta_0-1)=\delta(\hat{p}_0-\hat{K})$$

is established.

This result with Eq. 52 shows that

$$Q' \to \delta(p-p_0) + \frac{\sigma(\theta_0)}{D^2}\,\delta(p - p_0\hat{k}) \qquad (61)$$

$$- \frac{\Sigma}{D^2}\,\delta(\hat{p}_0 - \hat{k})\,\delta(p-p_0) \qquad (p_0 \neq 0.)$$

We have previously observed that Q' is the steady state distribution function describing a beam of particles with initial momentum p_0 scattered from a scattering center. This leads to a physical interpretation of the above expression for Q' at a large distance D from the scatterer. The first term in the expression for Q' represents the incident beam, the second term which falls off in intensity as D^{-2} represents the scattered beam, and the third term represents the shadow of the scatterer.

From Eqs. 27, 43, and 61 one finds that

$$\frac{16}{m}\int d\underline{r}\,dp\,p\cdot\frac{\partial}{\partial \underline{r}}\,\bar{f}^{(2)} = \frac{16}{m}\lim_{D\to\infty} D^2 \int d\hat{k}\,dp\,dp_0\,(\hat{k}\cdot p)$$

$$\times \bar{f}_1^{(1)}\bar{f}_2^{(1)}\left[\delta(p-p_0) + \frac{\sigma(\theta_0)}{D^2}\,\delta(p-p_0\hat{k}) - \frac{\Sigma}{D^2}\,\delta(p-p_0)\,\delta(\hat{p}_0-\hat{k})\right]. \qquad (62)$$

The term corresponding to the incident beam in this expression for the collision integral vanishes on integration over $\hat{k}$. The remaining δ-function integrations can then be carried out to obtain

$$\frac{16}{m}\int d\underline{x}\,d\underline{p}\;\underline{p}\cdot\frac{\partial}{\partial \underline{x}}\,\bar{f}^{(2)} = \frac{16}{m}\int d\hat{\underline{k}}\,d\underline{p}_0\,p_0\,\sigma(\vartheta_0)\,f^{(1)}\left(\underline{x}_1,\tfrac{1}{2}\underline{P}-p_0\hat{\underline{k}},t\right)$$

$$\times f^{(1)}\left(\underline{x}_1,\tfrac{1}{2}\underline{P}+p_0\hat{\underline{k}},t\right) - \frac{16}{m}\int d\underline{p}\;p\,\Sigma\,f^{(1)}(\underline{x}_1,\underline{p}_1,t)\,f^{(1)}(\underline{x}_1,\underline{p}_2,t). \qquad 63$$

If we change variables from p_0 to p in the first term and introduce the expression for the total cross section

$$\Sigma = \int d\hat{\underline{k}}\;\sigma(\vartheta) \qquad 64$$

into the second, we have

$$\frac{16}{m}\int d\underline{x}\,d\underline{p}\;\underline{p}\cdot\frac{\partial}{\partial \underline{x}}\,\bar{f}^{(2)} = \frac{16}{m}\int d\hat{\underline{k}}\,d\underline{p}\;p\,\sigma(\vartheta)$$

$$\times\left[f^{(1)}\left(\underline{x}_1,\tfrac{1}{2}\underline{P}-p\hat{\underline{k}},t\right)f^{(1)}\left(\underline{x}_1,\tfrac{1}{2}\underline{P}+p\hat{\underline{k}},t\right) - f^{(1)}(\underline{x}_1,\underline{p}_1,t)\,f^{(1)}(\underline{x}_1,\underline{p}_2,t)\right] \qquad 65$$

where $\cos\vartheta = \hat{\underline{p}}\cdot\hat{\underline{k}}$. This expression may be rewritten in the form

$$\int d\hat{\underline{k}}\,d\underline{p}_2\;v\,\sigma(\vartheta)\left[f^{(1)}\left(\underline{x}_1,\tfrac{1}{2}\underline{P}-p\hat{\underline{k}},t\right)f^{(1)}\left(\underline{x}_1,\tfrac{1}{2}\underline{P}+p\hat{\underline{k}},t\right)\right.$$

$$\left. - f^{(1)}(\underline{x}_1,\underline{p}_1,t)\,f^{(1)}(\underline{x}_1,\underline{p}_2,t)\right] \qquad 66$$

where $v = \frac{2p}{m}$ is the relative velocity of the two particles and the integration is over the momentum of the second particle. This result is identical to the classical collision integral except that here $\sigma(\vartheta)$ is the quantum mechanical differential cross section.

It is doubtful that the corrections to the collision integral can be reduced to a form so closely analogous to the classical result. The reason is that the classical corrections involve the detailed dynamics of binary collisions through the quantities $\underline{r}'$ and $\underline{p}'$ which, as has been mentioned, have no close correspondent in the quantum theory. In analogy with this the quantum mechanical corrections involve a detailed knowledge of quantum mechanical binary collisions and probably can not be expressed in terms of relatively simple quantities such as the phase shifts. Thus any computation using these corrections would probably be lengthy.

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