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[22]Note that the field σ of Sec. II is related to σ_0 and σ_8 by $\sigma = (\sqrt{2}\,\sigma_0 + \sigma_8)/\sqrt{3}$. The orthogonal combination $(\sigma_0 - \sqrt{2}\,\sigma_8)/\sqrt{3}$ is invariant under $SU_2 \otimes SU_2$ transformations.
[23]We take this opportunity to correct some misprints in our previous work (Ref. 10). The cited letter has the following misprints. In Eq. (3) the fraction $\frac{3}{4}$ ought to be $\frac{4}{3}$. The right-hand side of the equation defining λ [one line after Eq. (5)] needs to be divided by $\hat{\xi}_0^3$. The quantity τ defined in the paragraph preceding Eq. (7) should be $\tau = -4(3f_1 + f_2)\mu_0^2/3\gamma^2$. (Note that in the present work we have changed the definition of τ by a factor of 4.) Equation (7) is supposed to be $\det\{\partial(\epsilon_0, \epsilon_8)/\partial(\xi_0, b)\} = 0$. In Phys. Rev. D 4, 1808 (1971) the coefficient A_2 of η_{08} in Table I has opposite sign to that listed. In Phys. Rev. D 4, 1815 (1971) the factors $\mu_0^2/\sqrt{3}$ in Eq. (2.23) should be simply μ_0^2.

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Time Delay in Quantum Scattering*

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A new definition of the time delay in the scattering of a quantum-mechanical wave packet is proposed. It has a broader domain of applicability than previous definitions. The average time delay for the scattering of a plane-wave train is evaluated. Applications of the result to the quantum theory of the second virial coefficient are given.

I. INTRODUCTION

The concept of time delay in quantum scattering was introduced by Eisenbud,[1] in connection with the scattering of a spherical wave packet with a given angular momentum (e.g., s wave). Let $\eta(E)$ denote the scattering phase shift as a function of energy, and let us choose units such that $\hbar = 1$. Then, according to Eisenbud, the time delay undergone by the center of the outgoing wave packet in the scattering process is given by

$$\Delta t = 2\frac{d\eta}{dE}\,. \tag{1}$$

Negative Δt corresponds to a time advance, rather than a delay.

This result was employed by Wigner[2] to give a physical interpretation of the energy dependence of η and of an inequality for $d\eta/dE$ that is related with causality. The time delay (1) would take large positive values close to resonances, corresponding to a temporary capture of the incident particle by the scatterer. However, causality would not ordinarily[3] allow Δt to assume arbitrarily large negative values. The connection with causality was recently reexamined in an indefinite-metric theory.[4]

Alternative derivations of (1), some of which are based on quite different definitions and interpretations of the time delay, have been given. A review of these treatments is given in Sec. II.

The result has also been extended by Froissart, Goldberger, and Watson[5] to the scattering of plane-wave packets. They found for the time delay of the scattered wave packet in the direction θ the expression

$$\Delta t = \frac{\partial}{\partial E}\arg f(E,\theta)\,, \quad \theta \neq 0 \tag{2}$$

where $f(E, \theta)$ denotes the total scattering amplitude in the direction θ; the result does not apply in the forward direction. A related spatial displacement of the center of the wave packet was also found.[5,6]

A new definition of the time delay for spherical wave packets, representing an extension of ideas due to Smith[7] and Goldberger and Watson,[8] has recently been proposed.[9,10] The resulting expression for the time delay is the expectation value of (1) over the energy spectrum of the incident wave packet. Its domain of applicability is considerably broader than that of (1) (cf. Sec. II).

In the present work the new definition is extended to the scattering of plane-wave packets. In Sec. III we evaluate the average time spent by such a wave packet within a spherical region in the absence of interaction. The result is readily interpreted in terms of the average time of flight for a classical free particle beam.

The average time delay in the scattering process is obtained in Sec. IV by reevaluating the expression of Sec. III in the presence of interaction. The main result, given by Eqs. (33)–(35), involves not only the expectation value of (2) over the energy spectrum of the incident wave packet, but also an average over all directions, weighted by the differential cross section. It also includes the contribution from the time delay in the forward direction, which is given by a different expression, due to the interference with the incident wave.

The physical interpretation of the result and its domain of applicability are discussed in Sec. V. In Sec. VI it is shown that the continuum contribution to the second virial coefficient of a quantum system is proportional to the average time delay associated with an energy distribution given by the canonical ensemble. As an illustration, the dominant term in the high-temperature second virial coefficient of a hard-sphere gas is evaluated.

II. DISCUSSION OF PREVIOUS TREATMENTS

One group of contributions to the theory of time delay[1,2,5,11–13] defines it in terms of the displacement of the "center" of a wave packet, although this concept has different meanings for different authors.

The derivation of (1) given by Wigner[2] employs as a substitute for a wave packet an incident beam that is the superposition of two monoenergetic beams of slightly different energies, as is sometimes done in discussions of group velocity. However, the corresponding outgoing wave represents not only the effect of the scattering, but also the decay of the excitation that was initially concentrated within the interaction region. For Wigner's incident beam, the latter effect can become of the same order of magnitude as the former near resonance, when the corresponding initial excitation within the scatterer becomes large.

For a true spherical wave packet, the result (1) has been derived[11,12] by identifying the center of the wave packet roughly with the location where the probability amplitude is largest. The method of stationary phase is employed to determine the centers of the incoming and outgoing wave packets thus defined. It is assumed that the energy spectrum of the incident wave packet is sufficiently narrow so that the variation of $d\eta/dE$ over the spectral width can be neglected. By suitable choice of the incident wave packet, the initial excitation within the interaction region can be rendered negligibly small.

However, even when all these conditions are satisfied, it does not necessarily follow that the center of the outgoing wave packet is time-delayed by the amount (1). In fact, the method of stationary phase leads to incorrect results if the wings of the energy spectrum do not fall off sufficiently rapidly. Thus, Gaussian wave packets may be employed, but not Lorentzian ones.[14,15] Furthermore, since the shape of a quantum-mechanical wave packet can change considerably even in free propagation, the above concept of "center" need not be a good indicator of the average position and may thus lose much of its significance.

It should also be emphasized that, under the conditions for which (1) may be employed, the time delay, even at resonance, is a very small effect,[14] in the following sense: The displacement of the center of the wave packet due to the time delay is much smaller than the uncertainty in position associated with the packet (a narrow energy spectrum corresponds to a broad wave packet in configuration space). It follows, in particular, that it would be difficult to detect deviations from causality by using this effect.[4]

In Brenig and Haag's treatment,[13] the center of the wave packet corresponds to the "center of mass," i.e., to the expectation value of $r=|\vec{r}|$. Choosing the origin of time so that $\langle r\rangle=\langle v\rangle t$ for the incident wave packet, where $\langle v\rangle$ is the expectation value of the velocity, they find that, for sufficiently large times, $\langle r\rangle=\langle v\rangle(t-\langle\Delta t\rangle)$ for the scattered wave packet. The average time delay $\langle\Delta t\rangle$ is obtained from (2) by averaging over the energy spectrum of the incident wave packet, as well as over directions. "Sufficiently large times" means t so large that (a) the scattered wave packet is effectively outside of the interaction region, so that it can be treated as free; and (b) $t\gg t_s$, where t_s, the spreading time of the wave packet, can be defined as the time for which the wave packet has attained twice its original width through the quantum-mechanical spreading effect. The latter is a very stringent requirement[16]; as is well known, the conditions prevailing in ordinary scattering experiments are such that the spreading effect can be neglected.[17]

A second group of contributions to the theory of time delay[7–10] originated from a new interpretation of this concept, proposed by Smith.[7] He defined it as the difference, for large r, between the time spent by the particle within a distance r of the scattering center and the same quantity in the absence of interaction. Smith considered only stationary scattering states. The sojourn time within a sphere of radius r in a stationary situation was defined by the ratio of the probability to find the particle inside it to the inward or outward flux through the surface. This leads again to the result (1).

Goldberger and Watson[8] extended this interpretation to spherical wave packets, in the special case of potential scattering.[18] The resulting expression for the time delay is the expectation value of (1) over the energy spectrum of the incoming wave packet.

The restriction to potential scattering is unnecessary; it suffices to assume that the interaction is probability-conserving.[9,10] In fact, this implies that the probability of finding the particle within a distance r of the scattering center at time t is given by

$$P(r,t)=\int_{-\infty}^{t}\Phi(r,t')dt', \tag{3}$$

where $\Phi(r,t)$ is the inward probability flux through a sphere of radius r, and the incoming wave packet is so normalized as to represent one incident particle for $t\to-\infty$. In units such that $\hbar=1$ and the particle mass $m=\frac{1}{2}$, the flux is given by

$$\Phi(r,t)=i\oint\left(\psi^*\frac{\partial\psi}{\partial r}-\psi\frac{\partial\psi^*}{\partial r}\right)r^2d\Omega, \tag{4}$$

where $\psi(\vec{r},t)$ is the wave function associated with the wave packet.

The average time spent by the particle within the sphere is

$$T(r)=\int_{-\infty}^{\infty}P(r,t)dt. \tag{5}$$

The time delay in the scattering process is defined by

$$\Delta t(r)=T(r)-T_0(r), \tag{6}$$

where $T_0(r)$ is the value of $T(r)$ in the absence of interaction, and r is large enough so that the interaction can be neglected at the distance r; say, $r\gtrsim R$, where R is a characteristic distance measuring the range of the interaction. We see that, indeed, the only basic assumption about the interaction is probability conservation, and that only quantities defined in the asymptotic domain $r\gtrsim R$, "outside" of the interaction region, are involved.

By evaluating (6) for a spherical (e.g., s-wave) wave packet, one finds[9,10] that the result contains an oscillating term as a function of r, which represents a quantum effect connected with the uncertainty principle for $\langle\Delta r\rangle$. Averaging over r to eliminate this oscillating term, one gets for the average time delay

$$\langle\Delta t\rangle=2\left\langle\frac{d\eta}{dE}\right\rangle_{\text{in}}, \tag{7}$$

where the right-hand side denotes the expectation value taken over the energy spectrum of the incoming wave packet.

In particular, for a sufficiently narrow energy spectrum, we may be able to neglect the variation of $d\eta/dE$ over the spectral width, and we then recover Eisenbud's expression (1) for the time delay. However, $\langle\Delta t\rangle$ does not necessarily represent a shift of the center of the outgoing wave packet (which may undergo appreciable distortion); it should rather be interpreted as an average collision time, in the above-defined sense. The domain of applicability of (7) is much broader than that of (1); it may be applied to any normalizable wave packet, and it yields the dependence of the result on the choice of the incident wave packet. By considering explicit examples, it can be shown[10] that (7), in contrast with (1), gives a reasonable account of the average time delay in all cases.

The expression (7) is valid for all $r\gtrsim R$; in particular, it would remain valid at distances so large that spreading effects become important, and it would then agree with Brenig and Haag's result.[13] However, (7) can already be applied for much smaller values of r, well within the range of ordinary scattering experiments (of course, the very definition of scattering implies that the observations must be made for $r\gtrsim R$).

We see, therefore, that the above interpretation of the time delay is not subject to the limitations found in previous treatments. Let us now extend the results to the scattering of plane wave packets.

III. AVERAGE FREE TIME OF FLIGHT

Let us consider a plane incident wave train[19]

$$\psi_0(z,t)=\int_0^{\infty}A(E)\exp[i(kz-Et)]\,dE, \tag{8}$$

where (in units $\hbar=2m=1$)

$$E=k^2. \tag{9}$$

The total incident flux per unit area associated with (8) is

$$\varphi_{\text{in}}=-i\int_{-\infty}^{\infty}\left(\psi_0^*\frac{\partial\psi_0}{\partial z}-\psi_0\frac{\partial\psi_0^*}{\partial z}\right)dt$$
$$=4\pi\int_0^{\infty}k|A(E)|^2\,dE. \tag{10}$$

The total incident flux on a sphere of radius r is therefore

$$F=\pi r^2\varphi_{\text{in}}\,, \tag{11}$$

and (3) must be replaced by

$$FP(r,t)=\int_{-\infty}^{t}\Phi(r,t')dt'\,, \tag{12}$$

where $\Phi(r,t)$ is still given by (4). The average time spent by an incident particle within the sphere in the absence of interaction is

$$T_0(r)=\int_{-\infty}^{\infty}P_0(r,t)dt\,, \tag{13}$$

where P_0 is obtained by replacing ψ by ψ_0 in (4) and (12).

Performing this substitution, we find

$$FP_0(r,t)=-4\pi i r^2\int_{-\infty}^{t}dt'\int_0^{\infty}dE\int_0^{\infty}dE'\,kA^*(E')A(E)g((k-k')r)\exp[-i(E-E')t']+\text{c.c.}\,, \tag{14}$$

where c.c. denotes the complex conjugate, and

$$g(\zeta)=\frac{1}{2i}\int_0^{\pi}\exp(i\zeta\cos\theta)\cos\theta\sin\theta\,d\theta=\frac{\sin\zeta-\zeta\cos\zeta}{\zeta^2}\,. \tag{15}$$

The time integration in (14) may be carried out with the help of

$$\lim_{\epsilon\to 0+}\int_{-\infty}^{t}\exp[-i(E-E'+i\epsilon)t']\,dt'=i\,\frac{\exp[-i(E-E')t]}{E-E'+i0}=i\exp[-i(E-E')t]\,\frac{\mathcal{P}}{E-E'}+\pi\delta(E-E')\,, \tag{16}$$

where $\mathcal{P}$ denotes the Cauchy principal value.

Since

$$g(\zeta)=\tfrac{1}{3}\zeta+O(\zeta^3)\,,\quad \zeta\to 0 \tag{17}$$

the δ function does not contribute in (14), and the Cauchy principal-value symbol may be omitted, yielding

$$FP_0(r,t)=4\pi r^2\int_0^{\infty}dE\int_0^{\infty}dE'\,kA^*(E')A(E)\frac{g((k-k')r)}{k^2-k'^2}\exp[-i(E-E')t]+\text{c.c.} \tag{18}$$

Substituting in (13) and performing the time integration, we get another δ function, which, together with (17), leads to

$$FT_0(r,t)=\tfrac{8}{3}\pi^2r^3\int_0^{\infty}|A(E)|^2dE\,. \tag{19}$$

The expectation value of the momentum in the incident wave train is

$$\langle\vec{p}\rangle=\left(\int_{-\infty}^{\infty}\psi_0^*\vec{p}\psi_0dz\right)\Big/\left(\int_{-\infty}^{\infty}\psi_0^*\psi_0dz\right)=\hat{z}\left(\int_{-\infty}^{\infty}k|A(E)|^2dE\right)\Big/\left(\int_0^{\infty}|A(E)|^2dE\right)$$
$$=\tfrac{1}{2}\langle v\rangle\,\hat{z}\,, \tag{20}$$

where $\langle v\rangle$ is the expectation value of the velocity (the particle mass is $m=\frac{1}{2}$ in our units) and $\hat{z}$ is the unit vector in the z direction. Taking into account (11) and (20), the result (19) finally becomes

$$T_0(r)=\frac{4}{3}\,\frac{r}{\langle v\rangle}\,. \tag{21}$$

This result for the average free time of flight through a sphere of radius r has a simple physical interpretation. Consider a homogeneous beam of classical particles traveling in the z direction with velocity v, and going through a sphere of radius r centered at the origin. A particle that crosses the (x,y) plane at a distance ρ from the center has a travel time $2(r^2-\rho^2)^{1/2}/v$ through the sphere. Since the fraction of such particles between ρ and $\rho+d\rho$ is $2\pi\rho d\rho/(\pi r^2)$, the classical average free time of flight through the sphere is

$$T_0^{(\text{class})}(r)=\frac{4}{r^2v}\int_0^{r}(r^2-\rho^2)^{1/2}\rho\,d\rho=\frac{4r}{3v}\,, \tag{22}$$

and v must be replaced by an average velocity if the beam is not monoenergetic.

IV. THE TIME DELAY

In the presence of interaction, the total wave function associated with the incident wave train (8) becomes

$$\psi(\vec{r}, t) = \psi_0(z, t) + \psi_s(\vec{r}, t)\,, \tag{23}$$

where the scattered wave packet $\psi_s(\vec{r}, t)$ is asymptotically given by

$$\psi_s(\vec{r}, t) \approx \frac{1}{r}\int_0^\infty A(E) f(E, \theta)\exp[i(kr - Et)]\,dE\,, \quad r \gtrsim R \tag{24}$$

where, as in Sec. II, R denotes a distance so large that the interaction may be neglected for $r \gtrsim R$ and (24) holds to a sufficiently good approximation.

We may then substitute (23) and (24) in (4) and (12), leading to

$$\begin{aligned} F[P(r,t) - P_0(r,t)] = -\int_{-\infty}^{t} dt' \int d\Omega \int_0^\infty dE \int_0^\infty dE' \exp[-i(E-E')t']\, kA(E)A^*(E') \\ \times\{r f(E,\theta)\exp[ir(k - k'\cos\theta)] \\ + r\cos\theta\, f^*(E',\theta)\exp[ir(k\cos\theta - k')] \\ + f(E,\theta) f^*(E',\theta)\exp[i(k-k')r]\} + \text{c.c.}\,, \end{aligned} \tag{25}$$

where $P_0(r, t)$ is the free-particle contribution (14), and we have neglected higher-order terms. Performing the time integration with the help of (16), we get

$$\begin{aligned} F[P(r,t) - P_0(r,t)] = -\pi \int d\Omega \int_0^\infty dE\, k\,|A(E)|^2 (r(1+\cos\theta)\{f(E,\theta)\exp[ikr(1-\cos\theta)] \\ + f^*(E,\theta)\exp[-ikr(1-\cos\theta)]\} + 2|f(E,\theta)|^2) \\ - i\mathcal{P}\int d\Omega \int_0^\infty dE \int_0^\infty dE' \exp[-i(E-E')t]\,\frac{A(E)A^*(E')}{E-E'} \\ \times\{r(k + k'\cos\theta) f(E,\theta)\exp[ir(k - k'\cos\theta)] \\ + r(k' + k\cos\theta) f^*(E',\theta)\exp[ir(k\cos\theta - k')] \\ + (k+k') f(E,\theta) f^*(E',\theta)\exp[i(k-k')r]\}\,. \end{aligned} \tag{26}$$

We now employ the well-known formula[20]

$$\exp(ikr\cos\theta) = \exp(i\vec{k}_0\cdot\vec{r}) = -(2\pi i/kr)[\delta(\Omega_0 - \Omega_r)\exp(ikr) - \delta(\Omega_0 + \Omega_r)\exp(-ikr)] + O(r^{-2})\,, \quad r\to\infty \tag{27}$$

where $\vec{k}_0 = k\hat{z}$, and Ω_0 and Ω_r denote the directions of $\vec{k}_0$ and $\vec{r}$, respectively. Substituting in (26) and evaluating the δ-function contributions (coming from $\theta = 0$ and $\theta = \pi$), we get

$$\begin{aligned} F[P(r,t) - P_0(r,t)] = -2\pi\int_0^\infty dE\, k\,|A(E)|^2 \left\{\int d\Omega\,|f(E,\theta)|^2 + \frac{2\pi i}{k}[f(E,0) - f^*(E,0)]\right\} \\ - i\mathcal{P}\int_0^\infty dE \int_0^\infty dE' A(E)A^*(E')\exp[-i(E-E')t] \\ \times\left\{\frac{\exp[i(k-k')r]}{k-k'}\left[\int d\Omega\, f(E,\theta) f^*(E',\theta) + 2\pi i\left(\frac{f(E,0)}{k'} - \frac{f^*(E',0)}{k}\right)\right]\right. \\ \left. - \frac{2\pi i}{k+k'}\left(\frac{f(E,\pi)}{k'}\exp[i(k+k')r] + \frac{f^*(E,\pi)}{k}\exp[-i(k+k')r]\right)\right\}\,. \end{aligned} \tag{28}$$

The optical theorem

$$\sigma_t(E) = \int |f(E,\theta)|^2 d\Omega = \frac{4\pi}{k}\,\mathrm{Im} f(E, 0)\,, \tag{29}$$

where σ_t is the total cross section, implies that the first integral vanishes identically and that the integrand of the second integral is regular at $E=E'$, so that the principal value sign may be removed. Integrating both sides of the resulting expression over t from $-\infty$ to ∞, and taking into account (5), (6), and (13), we get

$$F\Delta t(r)=4\pi i\int_0^\infty dE\,k\,|A(E)|^2\left\{\frac{\partial}{\partial E'}\left[\int f(E,\theta)f^*(E',\theta)d\Omega+2\pi i\left(\frac{f(E,0)}{k'}-\frac{f^*(E',0)}{k}\right)\right]\right\}_{E'=E}$$
$$-2\pi^2\int_0^\infty \frac{dE}{E}|A(E)|^2[f(E,\pi)\exp(2ikr)+f^*(E,\pi)\exp(-2ikr)], \qquad (30)$$

where the δ-function contribution in the first integral has been evaluated by l'Hospital's rule. Carrying out the differentiation and symmetrizing[21] the result with respect to E and E', we obtain

$$F\Delta t(r)=2\pi i\int_0^\infty dE\,k\,|A(E)|^2\int d\Omega\left[f(E,\theta)\frac{\partial f^*}{\partial E}(E,\theta)-f^*(E,\theta)\frac{\partial f}{\partial E}(E,\theta)\right]$$
$$+8\pi^2\int_0^\infty\frac{dE}{E}k\,|A(E)|^2\frac{\partial}{\partial E}[k\,\mathrm{Re}f(E,0)]$$
$$-2\pi^2\int_0^\infty\frac{dE}{E}|A(E)|^2[f(E,\pi)\exp(2ikr)+f^*(E,\pi)\exp(-2ikr)]. \qquad (31)$$

The last term in (31) (backscattering contribution) has an oscillatory r dependence that corresponds precisely to the terms in $\sin(2kr)$ and $\sin(2kr+2\eta_l)$ obtained[7,10] in a partial-wave analysis for angular momentum l. Just as was done for (7), we dispose of this term by averaging over a distance of the order of a de Broglie wavelength in r.

Taking into account (11) and the relation

$$\tfrac{1}{2}i\left(f\frac{\partial f^*}{\partial E}-f^*\frac{\partial f}{\partial E}\right)=|f|^2\frac{\partial}{\partial E}\arg f, \qquad (32)$$

we obtain the final expression for the *average time delay in the scattering process*

$$\langle\Delta t(r)\rangle=\langle\tau_r(E)\rangle_{\mathrm{in}}, \qquad (33)$$

where

$$\tau_r(E)=\frac{1}{\pi r^2}\left(\int|f(E,\theta)|^2\frac{\partial}{\partial E}\arg f(E,\theta)d\Omega+\frac{2\pi}{E}\frac{d}{dE}[k\,\mathrm{Re}f(E,0)]\right) \qquad (34)$$

and

$$\langle F(E)\rangle_{\mathrm{in}}=\frac{\int_0^\infty k|A(E)|^2F(E)dE}{\int_0^\infty k|A(E)|^2dE} \qquad (35)$$

denotes an average over the energy spectrum of the incident wave train, similar to that employed[10] in the derivation of (7).

In terms of the partial-wave expansion

$$f(E,\theta)=\sum_l\frac{(2l+1)}{2ik}\{\exp[2i\eta_l(E)]-1\}P_l(\cos\theta), \qquad (36)$$

the result (34) may be rewritten as

$$\pi r^2\tau_r(E)=\frac{\pi}{E}\sum_l(2l+1)2d\eta_l/dE. \qquad (37)$$

The inverse r^2 dependence of $\langle\Delta t(r)\rangle$ arises from the scattering probability and may be removed by a suitable normalization (cf. Sec. V).

V. DISCUSSION

The first term in (34), when substituted in (33), corresponds to a double average of the Froissart-Goldberger-Watson time delay (2), involving both the energy averaging (35) and an average over directions. The latter also has a simple interpretation. Since we are considering a single scatterer at the center of a sphere of radius r, the probability of scattering into an element of solid angle $d\Omega$ in the direction θ is given by

$$dP_s=\frac{(d\sigma/d\Omega)d\Omega}{\pi r^2}=\frac{|f(E,\theta)|^2}{\pi r^2}d\Omega, \qquad (38)$$

which is the weight function in the first integral of (34). In this sense, therefore, we can say that the "time delay at energy E in the direction θ" ($\theta\neq 0$), insofar as such a quantity can be defined, is given by $\partial\arg f(E,\theta)/\partial E$, in agreement with (2). However, the physical interpretation of the time delay corresponds to (6), and it is not necessarily related to the position of the center of the scattered wave packet.

The total probability of scattering for incident beam particles with energy E that hit the sphere is

$$P_s(E, r) = \int \frac{dP_s}{d\Omega}\, d\Omega = \frac{\sigma_t(E)}{\pi r^2} . \tag{39}$$

The quantity

$$\frac{\langle \Delta t(r)\rangle}{\langle P_s(E, r)\rangle} = \frac{\pi r^2 \langle \tau_r(E)\rangle_{\text{in}}}{\langle \sigma_t(E)\rangle_{\text{in}}} \tag{40}$$

is independent of r and provides a different measure of the time delay (corresponding to a conditional probability) that may be more convenient for some purposes.

The second term in (34) corresponds to the time delay in the forward direction. This is different from all other directions because of the interference between the incident and scattered beams for $\theta = 0$. In the case of light propagation in a medium containing many scatterers, this forward time delay gives rise to the change in the phase velocity, corresponding to the well-known relation[10] between the real refractive index and the real part of the forward scattering amplitude. Both this result and its counterpart, the optical theorem (29), arise from the subtle interference effects that take place in the forward direction.

The partial-wave expansion (37) also has a simple interpretation. As is well known,[22] the factor $(2l+1)\pi/E$ may be interpreted as the area of a circular zone associated with the lth partial wave in the incident beam, so that $(2l+1)\pi/(\pi r^2 E)$ is the corresponding fraction of the incident beam area hitting a sphere of radius r. Taking into account (7) and (33), we see that the time delay for the plane wave train may be regarded as the resultant of the time delays for all its partial-wave components.

The remarks made in Sec. II about the advantages and the domain of applicability of (7) may be repeated here. The result (33) is not restricted to nearly monoenergetic and specially shaped wave packets. It also includes the contribution from the forward time delay. Finally, it is valid at realistic distances from the scatterer, where (24) may be applied. This requires, in particular, that $kr \gg 1$ for all values of k that are significantly represented in the incident wave train.

VI. APPLICATIONS

It is well known[23] that the second virial coefficient of a system is related to the corresponding two-particle collision lifetime.[24] The results of Sec. IV allow us to exhibit this relationship in a particularly transparent form.

The second virial coefficient $B(T)$ is defined by the Kammerlingh Onnes virial expansion

$$pV = RT\left(1 + \frac{B(T)}{V} + \cdots\right) . \tag{41}$$

It was shown by Beth and Uhlenbeck[25] that, for Boltzmann statistics,

$$B = B_{\text{dis}} + B_{\text{con}} , \tag{42}$$

where B_{dis}, the contribution from discrete energy levels, is given by

$$B_{\text{dis}} = -\sqrt{2}\, N\lambda^3 \sum_l (2l+1) \sum_n \exp(-\beta E_{n,l}) , \tag{43}$$

and the continuum contribution B_{con} is given by

$$B_{\text{con}} = -\frac{\sqrt{2}}{\pi} N\lambda^3 \sum_l (2l+1) \int_0^\infty \exp(-k^2/k_0^2) \frac{d\eta_l}{dk}\, dk . \tag{44}$$

In the above expressions, N is the number of particles, $\beta = 1/K_B T$, $\lambda = \sqrt{4\pi\beta} = \sqrt{2\pi}/k_0$ is the thermal wavelength (in our units), and $E_{n,l}$ is the energy of the nth bound state with angular momentum l. For Bose-Einstein or Fermi-Dirac statistics, the sums over l are extended only to even or odd l values, respectively, and there are additional contributions[25] representing the effects of the statistics for an ideal gas.

Comparing (44) with (37), we see that

$$B_{\text{con}} = -\frac{N\lambda^3}{\sqrt{2}\,\pi} r^2 \int_0^\infty k\, |A(E)|^2 \tau_r(E) dE , \tag{45}$$

where

$$|A(E)|^2 = k \exp(-k^2/k_0^2) = \sqrt{E}\, \exp(-E/k_0^2) . \tag{46}$$

Thus, taking into account (33) and (35),

$$B_{\text{con}} = -\sqrt{2}\, N \frac{2\pi}{\lambda} r^2 \langle \Delta t(r)\rangle , \tag{47}$$

where the energy spectrum of the incident wave packet is given by (45).

We conclude that the continuum contribution to the second virial coefficient is proportional to the average time delay for a representative incident wave packet with an energy spectrum given by the Boltzmann distribution[26] (corresponding to the canonical ensemble). The physical interpretation of this result is obtained by regarding contributions to the partition function from each region of phase space as being weighted by the time the system spends in that region.[8,23]

We finally apply the above results to the evaluation of the dominant term in the high-temperature second virial coefficient of a hard-sphere gas. According to (45) and (46),

$$B=-\frac{\sqrt{2}}{\pi}N\lambda^3r^2\int_0^\infty k^3\tau_r(k)\exp(-k^2/k_0^2)dk\,, \qquad (48)$$

where the subscript has been omitted because there are no bound states in this case. Let a be the diameter of the spheres, which is also the radius of the equivalent hard-sphere interaction in relative coordinates. The high-temperature assumption means that $k_0a \gg 1$.

Under these conditions, both the domains $0 \leq ka \lesssim 1$ and $1 \ll ka \lesssim k_0a$ contribute to the integral (48), but the factor k^3 damps the low-frequency contributions and enhances the high-frequency ones, so that the dominant contribution comes from the high-frequency domain $ka \gg 1$, as can readily be shown by simple estimates. Thus, we have to evaluate the time delay (34) for high-frequency scattering by a hard sphere.

The high-frequency scattering amplitude for a hard sphere is given by different expressions[27] in different angular regions. There are three different regions to be considered. In the geometrical reflection region $(ka)^{-1/3} \ll \theta \leq \pi$, we have

$$f(k,\theta)=-\tfrac{1}{2}a\exp(-2ika\sin\tfrac{1}{2}\theta)\left(1+\frac{i}{2ka\sin^3(\frac{1}{2}\theta)}+\cdots\right),\quad (ka)^{-1/3}\ll\theta\leq\pi \qquad (49)$$

neglecting exponentially small surface-wave contributions. In the diffraction peak region $0 \leq \theta \ll (ka)^{-1/3}$, we have

$$f(k,\theta)=\tfrac{1}{2}ika^2\left\{2\frac{J_1(ka\theta)}{ka\theta}+e^{i\pi/3}(ka)^{-2/3}[1.9923\,J_0(ka\theta)+0.6706(ka)^{1/3}\theta J_1(ka\theta)+\cdots]\right\},\quad 0\leq\theta\ll(ka)^{-1/3} \qquad (50)$$

where the first term represents the forward diffraction peak. Finally, in the transition region between the above two regions, $f(k,\theta)$ is given by a more complicated expression[28] that interpolates smoothly between the values (49) and (50).

Splitting the angular integration in (34) in terms of the above-defined regions, we get, together with the last term of (34), a sum of four different contributions. It is convenient to employ the normalization (40) for the results. The total probability of scattering in this case is

$$P_s(E,r)=2\pi a^2/\pi r^2=2a^2/r^2\,,\quad ka\gg1\,. \qquad (51)$$

It follows from (34) and (49) that the contribution from the geometrical reflection region is

$$\frac{\tau_r(\text{reflection})}{P_s(E,r)}=-\frac{a}{3k}[1+O((ka)^{-5/3})]; \qquad (52)$$

From (50) and from the expression for $f(k,\theta)$ in the transition region,[28] we get

$$\frac{\tau_r(\text{diffraction})+\tau_r(\text{transition})}{\tau_r(\text{reflection})}=O((ka)^{-1})\,. \qquad (53)$$

The forward time delay [last term of (34)] follows from (50) for $\theta=0$:

$$\frac{\tau_r(\text{forward})}{P_s(E,r)}=-\frac{1.9923}{2\sqrt{3}}\frac{a}{k}(ka)^{-5/3}[1+O((ka)^{-2/3})]\,. \qquad (54)$$

Putting together all these results, we finally get

$$\frac{\tau_r(k)}{P_s(E,r)}=-\frac{a}{3k}[1+O((ka)^{-1})]\,,\quad ka\gg1\,. \qquad (55)$$

Since the particle velocity is $v=2k$ in our units, we see that (55) corresponds to a time advance of the expected order of magnitude for direct reflection at the surface of the sphere.

Substituting (55) and (51) in (48) and performing the integration, we finally get

$$B_{\text{dir}}=\tfrac{2}{3}\pi Na^3[1+O(\lambda/a)]\,,\quad \lambda/a\ll1 \qquad (56)$$

where the subscript indicates that this is the "direct" contribution to the high-temperature second virial coefficient of a hard-sphere gas. It has been shown[29] that the "exchange" contribution, arising from the Bose or Fermi statistics, is exponentially small at high temperatures.

The dominant term in (56) is just the total excluded volume, and it is identical with the classical result for the second virial coefficient of a hard-sphere gas. The first quantum correction is of order λ/a; both this term and higher-order quantum corrections have been previously evaluated[30] by a different method, involving the solution of a boundary-value problem for the diffusion Green's function. The present derivation relates the results with the average time delay. It is interesting to note that, while the forward diffraction peak is responsible for half the total cross section at high frequencies, it contributes only toward the quantum correction terms in the second virial coefficient.

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[17]Cf., e.g., Ref. 8, p. 65.

[18]The "more general derivation" given in Ref. 8, p. 492, actually refers to the Wigner or stationary phase method.

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