requirements of the Widom and Griffith relationships is probably coincidental. On the other hand, errors in the PVT measurements arising from gravitational effects are least for hydrogen, and this fact probably tends to enhance the reliability of the data.

The experimental value of the index δ for He^3 given in Fig. 1 (point m) was determined from the PVT measurements of Sherman[10] to be 3.4 ± 0.3. It is of interest to note that this is consistent with the Widom and Griffith relationships using the other measured values of the He^3 indices.

Finally, according to Griffith's second relationship, θ probably increases with Λ^*, but there is insufficient experimental evidence at present to make any meaningful comparisons.

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EHRENFEST'S THEOREM AND SCATTERING THEORY*

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Hirschfelder[1] has shown that the evaluation of the expectation value of the Heisenberg equation of motion for a stationary (bound) state leads to a class of identities that are generalizations of the virial theorem. The object of this note is to show that when nonstationary (scattering) states are used to compute the expectation value, a new class of identities results. These are generalizations of Ehrenfest's theorem in the same sense that Hirschfelder's "hypervirial" theorems are generalizations of the virial theorem.

We shall prove the extended Ehrenfest's theorem in a very general form and then shall specialize the theorem to apply to momentum transfer, energy transfer, and rotational excitation.

The momentum-transfer theorem we derive below was previously derived by Gerjuoy for two particular cases: elastic scattering of a particle by a potential,[2] and inelastic scattering of electrons by atomic hydrogen.[3] A concise derivation based on the properties of the S matrix was also given by Corinaldesi.[4]

Corinaldesi's treatment is closer to the method of derivation employed here; however, his considerations were limited to single-particle elastic potential scattering. Gerjuoy's derivation was carried out by an explicit calculation in a coordinate (Schroedinger) representation. Because of the consequent notational complexity, the generalization from e-H scattering to more complicated (many-particle) processes could only be inferred as "plausible." It was suggested[2] that the symbolic methods which characterize recent reformulations of scattering theory[5,6] were unsuited to problems of this type, and that "it probably will be necessary to essentially redo" the treatments of references 5 and 6.

The extended Ehrenfest theorem is derived below by a straightforward application of the symbolic method as developed for time-independent scattering theory.[5,6] The validity of the generalization of the momentum-transfer theorem from the two special cases mentioned above is established. A completely general proof of the extended Ehrenfest theorem is presented, in a form suitable for the discussion of other questions as well as momentum transfer. The derivation is valid not only for single-particle elastic potential scattering, or inelastic e-H scattering, but also for scattering by complex aggregates. A modification of the symbolic methods currently used in scattering theory therefore appears unnecessary.

To prove the basic theorem we shall use the notation of reference 5. We consider an operator, A, as yet unspecified. We wish to calculate the rate of change, induced by the scattering process, in the value of the observable represented by A. Since a determination of the net change in the value of A implies that A is measurable in the initial and final states, we shall assume that A commutes with H_0. The eigenvectors of H_0, which constitute the basis for representing the initial and final states, therefore are also eigenvectors of the operator A ($A\Phi_a = A_a\Phi_a$).

The expectation value of the Heisenberg equation of motion for A, in a particular scattering state, a, is

$$(\Psi_a^{(+)}, \dot{A}\Psi_a^{(+)}) = \left(\Psi_a^{(+)}, \frac{1}{i\hbar}[A, H_1]\Psi_a^{(+)}\right). \tag{1}$$

Expanding the right-hand side in terms of the eigenvectors H_0 and using (I 1.63) and (I 1.61) we obtain

$$\frac{1}{i\hbar}\sum_b \{(\Psi_a^{(+)}, A\Phi_b)(\Phi_b, H_1\Psi_a^{(+)}) - (\Psi_a^{(+)}, H_1 A\Phi_b)(\Phi_b, \Psi_a^{(+)})\} = \frac{2}{\hbar}\sum_b A_b \,\mathrm{Im}(\Psi_a^{(+)}, \Phi_b)T_{ba}$$

$$= \frac{2}{\hbar}\sum_b A_b \,\mathrm{Im}T_{ba}\left\{\delta_{ba} + \frac{T_{ba}^*}{E_a - i\epsilon - E_b}\right\}. \tag{2}$$

In the limit $\epsilon \to 0$, this becomes (I 1.57)

$$\frac{2}{\hbar}A_a \,\mathrm{Im}T_{aa} + \frac{2\pi}{\hbar}\sum_b A_b |T_{ba}|^2 \delta(E_b - E_a). \tag{3}$$

If A is a constant of the motion during the entire collision, and not only during the initial and final states, the commutator of A with H_1 is zero and all A_b's are equal to A_a. The expression in (3) (with the A's cancelled) then equals zero (optical theorem):

$$\frac{2}{\hbar}\mathrm{Im}T_{aa} + \frac{2\pi}{\hbar}\sum_b |T_{ba}|^2 \delta(E_b - E_a) = 0. \tag{4}$$

If A is not a constant of the motion during the collision, this last relation and Eq. (1) lead to

$$(\Psi_a^{(+)}, \frac{1}{i\hbar}[A, H_1]\Psi_a^{(+)})$$

$$= \frac{2\pi}{\hbar}\sum_b (A_b - A_a)|T_{ba}|^2 \delta(E_b - E_a)$$

$$= \sum_b (A_b - A_a) w_{ba}. \tag{5}$$

In the last line we have introduced w_{ba}, the rate at which the transition probability increases (I 1.67).

This is the generalization of Ehrenfest's theorem. It states that the rate at which A is changed by the scattering process can be determined (except for the factor $1/i\hbar$) by eval-

uating the expectation value, in the appropriate scattering state, of the matrix element of the commutator of A and H_1.

Various choices of A are now possible:

(1) If A is any constant of the motion (during the entire collision) then, as observed in connection with Eq. (3) above, we always obtain the optical theorem, Eq. (4).

(2) If A is the momentum operator of the incident system $\underline{P}$, and H_1 is a potential V, we find

$$(\Psi_a^{(+)}, (-\nabla V)\Psi_a^{(+)}) = \sum_b (\vec{P}_b - \vec{P}_a) w_{ba}. \quad (6)$$

The (vector) rate of momentum transfer per unit time is given by the right-hand side of Eq. (6). In the simplest case, elastic scattering, this is equal to the momentum-transfer cross section times pv, the product of the (conserved) magnitudes of the momentum and the velocity of the incident particle; that is, we are led to the form of the theorem derived in reference 2.

As written, however, Eq. (6) is more general than this; in this form, the identity is valid for arbitrary scattering processes. In each specific instance, it is only necessary to substitute the corresponding elements of the T matrix, evaluated in the appropriate basis.

(3) If A is chosen to be $\vec{P}^2/2m$, the kinetic-energy operator of the incident system, the right-hand side of Eq. (5) represents the net rate of energy transfer between the incident particle and the target. If H_1 is again replaced by the potential V, we find

$$\left(\Psi_a^{(+)}, \frac{1}{2mi\hbar}[\vec{P}^2, V]\Psi_a^{(+)}\right) = \left(\Psi_a^{(+)}, \frac{1}{2m}\{-\vec{P}\cdot(\nabla V) - (\nabla V)\cdot\vec{P}\}\Psi_a^{(+)}\right) = \frac{1}{2m}\sum_b (\vec{P}_b^{\,2} - \vec{P}_a^{\,2}) w_{ba}. \quad (7)$$

(4) To discuss rotational excitation of a target, say a molecular rotator, we replace A by the rotational energy operator of the target $\vec{J}^2 B$, where $\vec{J}$ is the angular momentum operator of the rotator. Specializing to the case of a quadrupole interaction, H_1 is replaced by Q, a tensor operator of rank two. The T matrix then has matrix elements only between states for which the eigenvalue of the rotator J changes by ± 2, and Eq. (5) can be put in the form[7,8]

$$\left(\Psi_{J,\alpha}^{(+)}, \frac{B}{i\hbar}[\vec{J}^2, Q]\Psi_{J,\alpha}^{(+)}\right) = \sum_\beta \{(E_{J+2} - E_J) w_{J+2,\beta;J,\alpha} - (E_J - E_{J-2}) w_{J-2,\beta;J,\alpha}\}. \quad (8)$$

Here we have assumed that the rotator is originally in the state of angular momentum J, corresponding to the rotational energy E_J, and the remaining quantum numbers are given by α and β.

We close with some general comments.

(1) Following the technique already used above, a number of formal identities can be derived. These will probably be quite useful in exhibiting the implications of the general theory. However, their utility for practical calculations depends on the ease and accuracy with which the left-hand side of Eq. (5) can be evaluated. An exact determination of this expression requires, of course, an exact knowledge of the scattering-state vector $\Psi_a^{(+)}$. It is not immediately obvious how useful an evaluation via the Born approximation, or one of the other approximations used in scattering calculations, will be.

(2) The sum in Eq. (5) is over a complete set of states and therefore includes all reactions that are possible as a result of the collision. In particular, if rearrangements are possible and A is measurable both in the original and rearranged channel, Eq. (5) is still valid. However, it is useful to distinguish explicitly between the original and rearranged channels. Considering only two channels, let H_0' and H_1' represent the decomposition of the Hamiltonian in the original channel, and H_0'' and H_1'' the corresponding decomposition in the rearranged channel, with a similar convention for the basis vectors in each channel.[9] Assuming that A is meaningful (measurable) in both channels, one can show[10] that the theorem takes the form

$$(\Psi_a^{(+)'}, \hat{A}\Psi_a^{(+)'}) = \left(\Psi_a^{(+)'}, \frac{1}{i\hbar}[A, H_1']\Psi_a^{(+)'}\right) = \sum_{''b''} (A_{''b''} - A_a) w_{''b''a}^{('',')} + \sum_{''b''} (A_{''b''} - A_a) w_{''b''a}^{('',')}. \quad (9)$$

Here the notation ''b'' means that the summa-

tion is extended only over those states that propagate asymptotically in each channel. The transition probabilities per unit time are defined by

$$w_{ba}^{(\beta,\alpha)} = \frac{2\pi}{\hbar} |(\Phi_b^{\beta}, H_1^{\beta} \Psi_a^{(+)\alpha})|^2 \delta(E_b - E_a). \quad (10)$$

(3) As a further generalization of Eq. (5), we note that if a scattering interaction is included in H_0^{β}, the Φ_b^{β} state vectors are replaced by $\Phi_b^{(-)\beta}$, the eigenvectors of H_0^{β} corresponding to an incoming scattered-wave boundary condition.

(4) An essential element in the derivation of the extended Ehrenfest's theorem was the restriction that the state vectors that constitute the basis must also be eigenvectors of the operator A. On the other hand, Ehrenfest's theorem requires the construction of a wave packet. The ensuing contradiction is only apparent. It may be resolved by noting that if the scattering forces are zero outside a finite range, the wave packet may be constructed of free-particle states. To calculate the left-hand side of Eq. (5) and the matrix elements T_{ba}, the form of the wave packet is required only in the (finite) region where the potential differs from zero. In any such limited region we may go to the limit where the sum over free-particle states that constitutes the wave packet is replaced by a single, free-particle state.

When short- and long-range forces are both present, the long-range forces are first eliminated by constructing the wave packet as a superposition of the states corresponding to motion in the presence of the long-range forces. Within the short range of the remaining forces, the wave packet again may be replaced by just one of the superposed, long-range force states.

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