Hypervirial Theorem for Collisions between Electrons and Atoms*

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(Received 28 March 1963)

The hypervirial theorem was first introduced for bound-state systems and, subsequently, extended to one-electron scattering problems. In this paper electron-atom collisions are considered and the appropriate form of the hypervirial theorem is derived. Its relation to the original formulation is discussed. Application is made to the electron-hydrogen problem. Both elastic and inelastic collisions are investigated.

I. INTRODUCTION

THE classical and quantum-mechanical hypervirial theorems were first derived by Hirschfelder[1] for bound-state systems. From them an infinite family of exact relations may be deduced, the usual virial theorem being a particular member of this class. Some applications of the hypervirial relations have already been discussed.[2–4] Classically, they are useful in determining the equation of state for liquids; quantum mechanically, they are useful, among other things, in determining the constants in an approximate wave function and in improving expectation values.

Recently, Robinson and Hirschfelder[5] have shown that hypervirial theorems may also be derived for free systems. They considered the simplest possible scattering problem, the scattering of electrons by a central potential. Both classical and quantal formalisms were employed and in some instances the compatibility of corresponding results was demonstrated using the semiclassical approximation. Epstein and Robinson[6] have also reported that variational wave functions, optimized in accordance with Kohn's variational principle,[7] satisfy hypervirial theorems. Consequently, such theorems should be useful in selecting such approximate functions in order to obtain accurate phase shifts or scattering amplitudes.

The object of the present paper is to extend the hypervirial theorem to situations in which the scattering center has an internal structure. In Sec. II the theory is developed in general terms for collisions between electrons and N-electron atoms. The specific applications discussed in the subsequent sections are to the electron-hydrogen problem. In Sec. III exchange effects are neglected and some relations derived for elastic collisions. The effects of the Pauli principle are discussed in Sec. IV and analogous relations derived. More complicated inelastic collisions are investigated in Sec. V, exchange effects being first neglected, then included.

Atomic units are used throughout.

II. THEORY

The hypervirial theorem for systems obeying the laws of classical mechanics was derived using the classical equation of motion in terms of the Poisson brackets. The quantum-mechanical equivalent was derived using the Heisenberg equation of motion.[1] Consider an atomic system consisting of $N+1$ electrons labeled by subscripts i. The wave functions $\Psi(\mathbf{r}_1\cdots,\mathbf{r}_{N+1},t)$ describing this system satisfy the usual Schrödinger time-independent equation

$$H\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_{N+1},t)=E\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_{N+1},t), \quad (1)$$

with

$$H=-\tfrac{1}{2}\sum_{i=1}^{N+1}\nabla_i^2+V(\mathbf{r}_1,\cdots,\mathbf{r}_{N+1}), \quad (2)$$

where V denotes the total electrostatic potential energy.

Suppose W is an arbitrary time-independent operator and Ψ_m, Ψ_n are eigenfunctions satisfying Eq. (1) with eigenenergies E_m and E_n. Then[8]

$$\frac{d}{dt}\int\Psi_m^*W\Psi_n d\tau=-i\int\Psi_m^*[W,H]\Psi_n d\tau$$
$$=i(E_m-E_n)\int\Psi_m^*W\Psi_n d\tau. \quad (3)$$

Except where otherwise stated, it is to be assumed that the volume integration is over the volume space of all the electrons.

For bound systems the falloff with distance in the wave functions is usually sufficiently rapid to ensure a finite value for the expectation value of W. Consequently,

$$\int\Psi_n^*[W,H]\Psi_n d\tau=0. \quad (4)$$

This is the hypervirial theorem for bound-state systems.[1] The hypervirial relations are deduced by allow-

* This research was supported jointly by the following grant and contract: National Aeronautics and Space Administration Grant NsG–275–62(4180) and United States Air Force Contract AF 33(657)–7311.

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[5] P. D. Robinson and J. O. Hirschfelder, Phys. Rev. **129**, 1391 (1963).
[6] S. T. Epstein and P. D. Robinson, Phys. Rev. **129**, 1396 (1963).
[7] W. Kohn, Phys. Rev. **74**, 1763 (1948).
[8] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., p. 140.

ing the operator W to assume specific values. In scattering problems, however, the expectation value of W will not, in general, be finite. This is demonstrated in the Appendix for scattering of an electron by a central potential. Consequently, an alternative derivation for the hypervirial theorem must be used.

We note that if Ψ_1 and Ψ_2 are degenerate solutions of the Schrödinger equation (1) with associated eigenvalue E, then

$$(H-E)\Psi_1=(H-E)\Psi_2=0. \tag{5}$$

Hence,

$$\int W\Psi_2(H-E)\Psi_1 d\tau=\int \Psi_1 W(H-E)\Psi_2 d\tau. \tag{6}$$

Consider now

$$\int \Psi_1[H-E, W]\Psi_2 d\tau=\int \Psi_1(H-E)(W\Psi_2)d\tau - \int \Psi_1 W(H-E)\Psi_2 d\tau. \tag{7}$$

Using (6), the right-hand side of (7) may be rewritten as

$$\int \Psi_1(H-E)W\Psi_2 d\tau-\int (W\Psi_2)(H-E)\Psi_1 d\tau = \int \{\Psi_1 H(W\Psi_2)-(W\Psi_2)H\Psi_1\}d\tau \tag{8}$$

and since

$$\int \Psi_1 V(\mathbf{r}_1,\cdots,\mathbf{r}_{N+1})W\Psi_2 d\tau = \int (W\Psi_2)V(\mathbf{r}_1,\cdots,\mathbf{r}_{N+1})\Psi_1 d\tau, \tag{9}$$

we have

$$\int \Psi_1[H-E, W]\Psi_2 d\tau = -\tfrac{1}{2}\sum_i \int \{\Psi_1\nabla_i^2(W\Psi_2)-(W\Psi_2)\nabla_i^2\Psi_1\}d\tau. \tag{10}$$

Assuming that $W\Psi_2$ is a well-behaved function throughout the space $\mathbf{r}_i$, so that Green's theorem can be applied, we obtain

$$\int \{\Psi_1\nabla_i^2(W\Psi_2)-(W\Psi_2)\nabla_i^2\Psi_1\}d\tau = \int d\tau_i'\int_{S_i}\{\Psi_1\nabla_i(W\Psi_2)-(W\Psi_2)\nabla_i\Psi_1\}\cdot d\mathbf{S}_i, \tag{11}$$

where the volume space τ_i' refers to the space of all the electrons other than electron i. This enables us to write the hypervirial theorem in the form

$$\int \Psi_1[H-E, W]\Psi_2 d\tau = -\tfrac{1}{2}\sum_i \int d\tau_i'\int_{S_i}\{\Psi_1\nabla_i(W\Psi_2)-(W\Psi_2)\nabla_i\Psi_1\}\cdot d\mathbf{S}_i. \tag{12}$$

If W commutes with E, then this reduces to

$$\int \Psi_1[H,W]\Psi_2 d\tau = -\tfrac{1}{2}\sum_i \int d\tau_i'\int_{S_i}\{\Psi_1\nabla_i(W\Psi_2)-(W\Psi_2)\nabla_i\Psi_1\}\cdot d\mathbf{S}_i. \tag{13}$$

In the subsequent sections these relations will be applied to electron-hydrogen collisions. In this case they become

$$\int\int \Psi_1[H-E, W]\Psi_2 d\tau = -\frac{1}{2}\int d\tau_1\int_{S_2}\{\Psi_1\nabla_2(W\Psi_2)-(W\Psi_2)\nabla_2\Psi_1\}\cdot d\mathbf{S}_2 - \frac{1}{2}\int d\tau_2\int_{S_1}\{\Psi_1\nabla_1(W\Psi_2)-(W\Psi_2)\nabla_1\Psi_1\}\cdot d\mathbf{S}_1 \tag{12'}$$

and

$$\int\int \Psi_1[H,W]\Psi_2 d\tau = -\frac{1}{2}\int d\tau_1\int_{S_2}\{\Psi_1\nabla_2(W\Psi_2)-(W\Psi_2)\nabla_2\Psi_1\}\cdot d\mathbf{S}_2 - \frac{1}{2}\int d\tau_2\int_{S_1}\{\Psi_1\nabla_1(W\Psi_2)-(W\Psi_2)\nabla_1\Psi_1\}\cdot d\mathbf{S}_1. \tag{13'}$$

III. ELASTIC SCATTERING WITHOUT EXCHANGE

The wave equation for the system, incident electron plus target hydrogen atom, is

$$\{\nabla_1^2+\nabla_2^2+2E+2/r_1+2/r_2-2/r_{12}\}\Psi(\mathbf{r}_1,\mathbf{r}_2)=0, \tag{14}$$

where the incident electron is distinguished by the suffix 1, the atomic electron by the suffix 2. For the time being, the effects of electron exchange are neglected.

We may expand the wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ in the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=S_n\psi_n(\mathbf{r}_2)F_n(\mathbf{r}_1). \tag{15}$$

Here the large S indicates summation over discrete states and integration over the continuum. The functions $\psi_n(\mathbf{r}_2)$ are solutions of the Schrödinger equation

for a hydrogen atom:

$$\{\nabla_2^2+2\epsilon_n+2/r_2\}\psi_n(\mathbf{r}_2)=0. \tag{16}$$

Substituting (15) in (14) and using (16) gives

$$\{\nabla_1^2+k_n^2\}F_n(\mathbf{r}_1) =2\int\left(\frac{1}{r_{12}}-\frac{1}{r_1}\right)\Psi(\mathbf{r}_1,\mathbf{r}_2)\psi_n^*(\mathbf{r}_2)d\tau_2, \tag{17}$$

where k_n is the wave number for a free particle with energy $(E-\epsilon_n)$ and is defined by

$$k_n^2=2(E-\epsilon_n). \tag{18}$$

Now, substituting for Ψ, using (15), in (17) we obtain an infinite set of coupled equations for $F_n(\mathbf{r}_1)$:

$$\{\nabla_1^2+k_n^2\}F_n(\mathbf{r}_1)=2S_mU_{nm}F_m(\mathbf{r}_1), \tag{19}$$

where

$$U_{nm}=\int\psi_n^*(\mathbf{r}_2)\left(\frac{1}{r_{12}}-\frac{1}{r_1}\right)\psi_n(\mathbf{r}_2)d\tau_2. \tag{20}$$

We require solutions to (19) subject to the asymptotic conditions

$$\begin{aligned} &F_n(\mathbf{r}_1)\sim r_1^{-1}e^{ik_nr_1}f_n(\theta_1,\phi_1), && n\neq 0\\ &F_n(\mathbf{r}_1)\sim e^{i\mathbf{k}_0\cdot\mathbf{r}_1}+r_1^{-1}e^{ik_0r_1}f_0(\theta_1,\phi_1), && n=0. \end{aligned} \tag{21}$$

To solve (19) it is necessary to use some approximate method of procedure. In the distorted-wave approximation nondiagonal matrix elements are assumed small and on the right-hand side of (19), all matrix elements, except those associated with the initial state $m=0$, are neglected. This gives

$$\begin{aligned} &\{\nabla_1^2+k_n^2-2U_{nn}\}F_n(\mathbf{r}_1)=2U_{n0}F_0(\mathbf{r}_1),\\ &\{\nabla_1^2+k_0^2-2U_{00}\}F_0(\mathbf{r}_1)=0. \end{aligned} \tag{22}$$

The first of Eqs. (22) is equivalent to taking

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2)+F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2) \tag{23}$$

in (17); the second is equivalent to taking

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2) \tag{24}$$

in the corresponding equation for F_0. The Born approximation is equivalent to replacing $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ in (17) by a plane wave $e^{i\mathbf{k}_0\cdot\mathbf{r}_1}$. It is interesting to note that if the distorted-wave approximation is valid then the elastic scattering is the same as that due to a static center of force with potential[9] U_{00}.

We shall now derive hypervirial relations for elastic scattering assuming the wave functions to be given by (24). The major concern is to choose values for the operator W such that the right-hand sides of Eqs. (12′) and (13′) are finite. Following Robinson and Hirschfelder, we first of all choose

$$W=r_1\frac{\partial}{\partial r_1}-k_0\frac{\partial}{\partial k_0}, \tag{25}$$

and since W in this case does not commute with the energy E, we use the hypervirial in the form (12′). We assume the degenerate eigenfunctions for the complete system are $\Psi_1(\mathbf{r}_1,\mathbf{r}_2)$ and $\Psi_2(\mathbf{r}_1,\mathbf{r}_2)$ defined by

$$\Psi_i(\mathbf{r}_1,\mathbf{r}_2)=F_0^{(i)}(\mathbf{r}_1)\psi_0(\mathbf{r}_2), \tag{26}$$

with asymptotic form

$$\Psi_i\sim\{e^{i\mathbf{k}_0^{(i)}\cdot\mathbf{r}_1}+r_1^{-1}e^{ik_0^{(i)}r_1}f_0(\theta^{(i)},\phi^{(i)})\}\psi_0(\mathbf{r}_2) \tag{27}$$

for large r_1. Since the eigenfunctions are degenerate we know that the vectors $\mathbf{k}_0^{(1)}$ and $\mathbf{k}_0^{(2)}$ have equal magnitude, k_0, but different directions. Consider now the right-hand side of (12′). The first term is trivially zero due to the fast falloff for $\psi_0(\mathbf{r}_2)$. The second term must be more carefully examined. Consider first the integral over the surface S_1 at infinity. Since the operator W acts only on $F_0^{(2)}$ we can rewrite this as

$$\lim_{S_1\to\infty}\int_{S_1}\{WF_0^{(2)}\nabla_1F_0^{(1)}-F_0^{(1)}\nabla_1WF_0^{(2)}\}\cdot d\mathbf{S}_1 \tag{28}$$

and use the asymptotic forms for the F's defined by (27). We obtain

$$WF_0^{(2)}\frac{\partial F_0^{(1)}}{\partial r_1}-F_0^{(1)}\frac{\partial}{\partial r_1}(WF_0^{(2)})=\exp[ik_0r_1(1+\cos\theta^{(1)})] \times\frac{d}{dk_0}[k_0f_0(\theta^{(2)})]\{ik_0r_1^{-1}(1-\cos\theta^{(1)})-r_1^{-2}\}. \tag{29}$$

Proceeding now in a manner similar to that outlined in the Appendix we find

$$\int_{S_1}\{WF_0^{(2)}\nabla_1F_0^{(1)}-F_0^{(1)}\nabla_1WF_0^{(2)}\}\cdot d\mathbf{S}_1 =-4\pi\frac{d}{dk_0}[k_0f_0(\pi-\gamma)], \tag{30}$$

where γ is the angle between $\mathbf{k}_0^{(1)}$ and $\mathbf{k}_0^{(2)}$. The volume integration gives unity, since $\psi_0(\mathbf{r}_2)$ is assumed normalized. Hence, we have

$$\int\int\psi_0(\mathbf{r}_2)F_0^{(1)}(\mathbf{r}_1)[H-E,\,W]\psi_0(\mathbf{r}_2)F_0^{(2)}(\mathbf{r}_1)d\tau_1d\tau_2 =-2\pi\frac{d}{dk_0}[k_0f_0(\pi-\gamma)]. \tag{31}$$

We note that using (18),

$$[H-E,\,W]\Psi=-\left\{\nabla_1^2+k_0^2+r_1\frac{\partial V}{\partial r_1}\right\}\Psi, \tag{32}$$

[9] H. S. W. Massey, in *Handbuch Der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 26, Atoms II.

where V is the potential energy defined by

$$V=-1/r_1-1/r_2+1/r_{12}. \tag{33}$$

Hence, (31) may be rewritten in the form

$$\int\int\psi_0(\mathbf{r}_2)F_0^{(1)}(\mathbf{r}_1)\times\left[\nabla_1^2+k_0^2+r_1\frac{\partial V}{\partial r_1}\right]\psi_0(\mathbf{r}_2)F_0^{(2)}(\mathbf{r}_1)d\tau_1 d\tau_2=2\pi\frac{d}{dk_0}[k_0 f_0(\pi-\gamma)] \tag{34}$$

and using (22) and (20) may be further simplified to give

$$\int F_0^{(1)}(\mathbf{r}_1)\left[2U_{00}+r_1\frac{\partial U_{00}}{\partial r_1}\right]F_0^{(2)}(\mathbf{r}_1)d\tau_1=2\pi\frac{d}{dk_0}[k_0 f_0(\pi-\gamma)]. \tag{35}$$

This is exactly the hypervirial relation derived by Robinson and Hirschfelder[5] for scattering by a central potential U_{00}. It had also been previously derived by Demkov[10] using Hulthén's variational principle and constitutes the usual virial relation. It is instructive to consider the particular case where $\Psi_1=\Psi_2^*$. Then $\gamma=\pi$ and (35) reduces to

$$\int F_0^*(\mathbf{r}_1)\left[2U_{00}+r_1\frac{\partial U_{00}}{\partial r_1}\right]F_0(\mathbf{r}_1)d\tau_1=2\pi\frac{d}{dk_0}[k_0 f_0(0)]. \tag{36}$$

This might be interesting in certain connections if used in conjunction with the theorem which states that the total elastic cross section is equal to $4\pi/k_0$ times the imaginary part of the forward scattering amplitude $f_0(0)$. It is also important in that it provides a check on our general derivation of the hypervirial theorem since (36) was previously derived by Robinson and Hirschfelder[5] for one particle scattering by a central potential.

It should also be pointed out that any choice of operator W which yields convergent integrals for central potential scattering should also do so in the present context. Consequently, we might adopt for W powers of $(r_1\partial/\partial r_1-k_0\partial/\partial k_0)$ or $r_1e^{-\alpha r_1}\partial/\partial r_1$. With the latter choice for W both the surface integrals in (12′) are found to be zero. An entire family of such operators is available, and each can be used to generate a new hypervirial relation.

IV. ELASTIC SCATTERING INCLUDING EXCHANGE

The form of the wave function in the theory of elastic scattering including exchange is usually approximated in the following manner.[9] We have seen in (15) that the total wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ can be expanded in the form

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+\Phi(\mathbf{r}_1,\mathbf{r}_2), \tag{37}$$

where $\Phi(\mathbf{r}_1,\mathbf{r}_2)$ represents the totality of all the scattering waves. Alternatively, we might expand $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=S_nG_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1),$$

where $G_n(\mathbf{r}_2)$ has the asymptotic form

$$G_n(\mathbf{r}_2)\sim r_2^{-1}e^{ik_nr_2}g_n(\theta_2)\quad(r_2\text{ large}). \tag{38}$$

If we now expand $\Phi(\mathbf{r}_1,\mathbf{r}_2)$ in the form

$$\Phi(\mathbf{r}_1,\mathbf{r}_2)=S_nG_n'(\mathbf{r}_2)\psi_n(\mathbf{r}_1), \tag{39}$$

we should expect[9] that $G_0\approx G_0'$ and we might write

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)+F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+\phi. \tag{40}$$

Neglecting ϕ we should have a fair approximation to the total wave function. It is well known[9] that the differential cross section for elastic collisions independent of the approximation is defined by

$$I(\theta)=\tfrac{3}{4}|f_0(\theta)+g_0(\theta)|^2+\tfrac{1}{4}|f_0(\theta)-g_0(\theta)|^2, \tag{41}$$

the weighting factors 3:1 being a consequence of the Pauli principle.

We shall now consider the derivation of particular relations assuming the total wave function to be adequately represented by (40). Choosing $W'=r_1\partial/\partial r_1-k_0\partial/\partial k_0$ as before, the integral over the surface S_2 is found to be infinite. Instead, we use a symmetrized form for W given by

$$W_S=r_1\frac{\partial}{\partial r_1}+r_2\frac{\partial}{\partial r_2}-k_0\frac{\partial}{\partial k_0}. \tag{42}$$

Also, for simplicity we assume

$$\Psi_1(\mathbf{r}_1,\mathbf{r}_2)=\Psi_2(\mathbf{r}_1,\mathbf{r}_2)=\Psi(\mathbf{r}_1,\mathbf{r}_2). \tag{43}$$

A. Integration over S_2

Substituting in (12′) we find that the integral over the surface S_2 is given by

$$\int_{S_2}\{[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]\times\nabla_2W_S[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]-W_S[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]\times\nabla_2[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]\}\cdot d\mathbf{S}_2. \tag{44}$$

Because of the asymptotic form of $\psi_0(\mathbf{r}_2)$ this reduces to

$$\int_{S_2}\{G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)\nabla_2W_S[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]-W_S[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]\nabla_2[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)]\}\cdot d\mathbf{S}_2. \tag{45}$$

[10] Y. N. Demkov, Dokl. Akad. Nauk S.S.S.R. **89**, 249 (1953).

Similarly, the integral over the surface S_1 becomes

$$\int_{S_1}\{F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\nabla_1 W_S[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)] - W_S[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]\nabla_1[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]\}\cdot d\mathbf{S}_1. \quad (46)$$

Consider now the integral (45). Using the form of $G_0(\mathbf{r}_2)$ given by (38) we obtain

$$\frac{\partial}{\partial r_2}[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)] = \psi_0(\mathbf{r}_1)[ik_0 r_2^{-1}e^{ik_0 r_2}g_0(\theta_2) - r_2^{-2}e^{ik_0 r_2}g_0(\theta_2)]. \quad (47)$$

Also,

$$\left(r_2\frac{\partial}{\partial r_2} - k_0\frac{\partial}{\partial k_0}\right)[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)] = -\psi_0(\mathbf{r}_1)r_2^{-1}e^{ik_0 r_2}\left[g_0(\theta_2) + k_0\frac{\partial g_0}{\partial k_0}\right] \quad (48)$$

and

$$r_1\frac{\partial}{\partial r_1}[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)] = r_1 G_0(\mathbf{r}_2)\frac{\partial\psi_0}{\partial r_1}. \quad (49)$$

Hence,

$$W_S[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)] = r_2^{-1}e^{ik_0 r_2}\left\{r_1\frac{\partial\psi_0}{\partial r_1}g_0 - \psi_0(\mathbf{r}_1)g_0(\theta_2) - k_0\psi_0(\mathbf{r}_1)\frac{\partial g_0}{\partial k_0}\right\} \quad (50)$$

and

$$\frac{\partial}{\partial r_2}W_S[G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)] = \left\{r_1\frac{\partial\psi_0}{\partial r_1}g_0(\theta_2) - \psi_0(\mathbf{r}_1)g_0(\theta_2) - k_0\psi_0(\mathbf{r}_1)\frac{\partial g_0}{\partial k_0}\right\} \times\{ik_0 r_2^{-1}e^{ik_0 r_2} - r_2^{-2}e^{ik_0 r_2}\}. \quad (51)$$

Substituting now in (45) using (47), (50), and (51) and noting that terms of order r_2^{-3} and r_2^{-4} vanish in limit of large r_2, we find that (45), the integration over S_2, is identically zero.

B. Integration over S_1

Consider now (46). If we define

$$W' = r_1\frac{\partial}{\partial r_1} - k_0\frac{\partial}{\partial k_0}, \quad (52)$$

the integration over S_1, using $W_S = W' + r_2\partial/\partial r_2$, may be rewritten as

$$\int_{S_1}\Big\{F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\nabla_1 W'[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)] + F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)r_2\frac{\partial}{\partial r_2}\nabla_1[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)] - W'[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]\nabla_1[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)] - r_2F_0(\mathbf{r}_1)\frac{\partial\psi_0}{\partial r_2}\nabla_1[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]\Big\}\cdot d\mathbf{S}_1 \quad (53)$$

and, consequently, reduces to

$$\int_{S_1}\{F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\nabla_1 W'[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)] - W'[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]\nabla_1[F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)]\}\cdot d\mathbf{S}_1. \quad (54)$$

Using (30) we now obtain for (44), the integration over S_1,

$$+4\pi\frac{d}{dk_0}[k_0 f_0(\pi)]. \quad (55)$$

Thus, the hypervirial relation corresponding to W_S is

$$\int\int\Psi(\mathbf{r}_1,\mathbf{r}_2)\left\{\nabla_1^2 + k_0^2 + r_1\frac{\partial V}{\partial r_1} + r_2\frac{\partial V}{\partial r_2}\right\}\Psi(\mathbf{r}_1,\mathbf{r}_2)d\tau_1 d\tau_2 = 2\pi\frac{d}{dk_0}[k_0 f_0(\pi)]. \quad (56)$$

Provided it is properly symmetrized, any operator W used in Sec. III can also be used in the present discussion. Consequently, we can again deduce a family of hypervirial relations.

V. INELASTIC SCATTERING

We shall now show that the hypervirial theorem derived in Sec. II is applicable equally well to inelastic as to elastic collisions. We choose the approximate form

$$\Psi_i(\mathbf{r}_1,\mathbf{r}_2) = F_0^{(i)}(\mathbf{r}_1)\psi_0(\mathbf{r}_2) + F_n^{(i)}(\mathbf{r}_1)\psi_n(\mathbf{r}_2) \quad (57)$$

for the total wave function. As seen in Sec. III, this corresponds to using a distorted-wave approximation.

The integral over the surface S_2 in (12′) is again zero due to the rapid falloff in the bound-state hydrogen-atom wave functions. Also $\psi_0(\mathbf{r}_2)$ and $\psi_n(\mathbf{r}_2)$ are orthogonal. Hence, (12′) reduces to give

$$\int\int\Psi_1[H-E, W]\Psi_2 d\tau_1 d\tau_2 = \frac{1}{2}\int_{S_1}\{WF_0^{(2)}\nabla_1 F_0^{(1)} - F_0^{(1)}\nabla_1(WF_0^{(2)})\}\cdot d\mathbf{S}_1 + \frac{1}{2}\int_{S_1}\{WF_n^{(2)}\nabla_1 F_n^{(1)} - F_n^{(1)}\nabla_1(WF_n^{(2)})\}\cdot d\mathbf{S}_1. \quad (58)$$

In choosing a particular operator W we must be careful to ensure that both the surface integrals in (58) are convergent. Our choice is, in general, more restricted for inelastic collisions. For example, the operators

$$W = r_1\frac{\partial}{\partial r_1} \pm k_0\frac{\partial}{\partial k_0}, \quad r_1\frac{\partial}{\partial r_1} \pm k_n\frac{\partial}{\partial k_n}, \quad r_1\frac{\partial}{\partial r_1} \pm k_0\frac{\partial}{\partial k_0} \pm k_n\frac{\partial}{\partial k_n} \quad (59)$$

and all powers of these are now excluded. It is convenient instead to consider operators of the form

$$W=r_1e^{-\alpha r_1}\frac{\partial}{\partial r_1},\quad \alpha>0. \tag{60}$$

The exponential factor now ensures convergence and the surface integrals in (58) both give zero. To allow for exchange effects, we might write $\Psi(\mathbf{r}_1,\mathbf{r}_2)$ as

$$\Psi(\mathbf{r}_1,\mathbf{r}_2)=F_0(\mathbf{r}_1)\psi_0(\mathbf{r}_2)+F_n(\mathbf{r}_1)\psi_n(\mathbf{r}_2)+G_0(\mathbf{r}_2)\psi_0(\mathbf{r}_1)+G_n(\mathbf{r}_2)\psi_n(\mathbf{r}_1). \tag{61}$$

As before we can generate hypervirial relations by choosing properly symmetrized forms for the operators W.

It should be emphasized that although the hypervirial theorem (12) is exact, all the particular relations derived are approximate. The degree of accuracy is determined by the accuracy of approximate forms adopted for the total wave function $\Psi(\mathbf{r}_1,\mathbf{r}_2)$. In the present discussion we have used the distorted-wave approximation, but clearly analogous relations might be derived for any given approximate function.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor C. F. Curtiss for many helpful suggestions during the course of this investigation. Thanks are also due to other members of the Theoretical Chemistry Institute for numerous stimulating discussions.

APPENDIX

We wish to show that the integral

$$J=\int\Psi_1^*(\mathbf{r})W\Psi_2(\mathbf{r})d\tau \tag{A1}$$

is divergent, where $\Psi_1(\mathbf{r})$ and $\Psi_2(\mathbf{r})$ are degenerate wave functions with asymptotic form

$$\Psi_i(\mathbf{r})\sim\exp(ikr\cos\theta_i)+r^{-1}\exp(ikr)f(\theta_i) \tag{A2}$$

and

$$W=r\partial/\partial r-k\partial/\partial k. \tag{A3}$$

It will be sufficient to consider the integral (A1) over all space outside a sphere of radius R, where R is sufficiently large for the wave functions to assume their asymptotic forms. Then

$$W\Psi_2(\mathbf{r})=-r^{-1}\exp(ikr)\frac{\partial}{\partial k}[kf(\theta_2)] \tag{A4}$$

and

$$\Psi_1^*(\mathbf{r})W\Psi_2(\mathbf{r})=-r^{-1}\exp[ikr(1-\cos\theta_1)]\frac{\partial}{\partial k}[kf(\theta_2)]-r^{-2}f^*(\theta_1)\frac{\partial}{\partial k}[kf(\theta_2)]. \tag{A5}$$

We now expand $f(\theta)$ in a series of Legendre polynomials as

$$f(\theta)=\frac{1}{2ik}\sum_l(2l+1)[\exp(2i\eta_l)-1]P_l(\cos\theta), \tag{A6}$$

where η_l is the phase shift. Hence,

$$\frac{\partial}{\partial k}[kf(\theta_2)]=\sum_l(2l+1)\exp(2i\eta_l)\frac{\partial\eta_l}{\partial k}P_l(\cos\theta_2). \tag{A7}$$

Also

$$\exp(-ikr\cos\theta_1)=(kr)^{-1}\sum_l(2l+1)(-i)^l\sin(kr-\tfrac{1}{2}\pi l)P_l(\cos\theta_1). \tag{A8}$$

Thus,

$$-r^{-1}\exp[ikr(1-\cos\theta_1)]\frac{\partial}{\partial k}[kf(\theta_2)]=-kr^{-2}\exp(ikr)\sum_{l,l'}(2l+1)(2l'+1)(-i)^{l'}\exp(2i\eta_l)\frac{\partial\eta_l}{\partial k}\sin(kr-\tfrac{1}{2}\pi l')P_l(\cos\theta_2)P_{l'}(\cos\theta_1). \tag{A9}$$

In order to carry out the angular part of the integration we define a set of coordinates axes at 0, the scattering center, such that the coordinates of a point $\mathbf{r}$ on the unit sphere are (Θ,Φ). Denote by (Θ_i,Φ_i) the corresponding coordinates for the unit vectors $\hat{k}_i$. Then substituting in (A9) using

$$P_l(\cos\theta_i)=\frac{2}{2l+1}\sum_{m=-n}^{n}\bar{P}_l^m(\cos\Theta)\bar{P}_l^m(\cos\Theta_i)\exp[im(\Phi-\Phi_i)], \tag{A10}$$

where $\bar{P}_l^m$ is the normalized associated Legendre polynomial, we obtain

$$-\frac{4}{kr^2}\exp(ikr)\sum_{\substack{l,l'\\m,m'}}(-i)^{l'}\exp(2i\eta_l)\frac{\partial\eta_l}{\partial k}\sin(kr-\tfrac{1}{2}\pi l')\bar{P}_l^m(\cos\Theta)\bar{P}_{l'}^{m'}(\cos\Theta)\times\bar{P}_l^m(\cos\Theta_2)\bar{P}_{l'}^{m'}(\cos\Theta_1)\exp[im(\Phi-\Phi_2)]\exp[im'(\Phi_1-\Phi)]. \tag{A11}$$

Integrating now over Θ and Φ, only $l'=l$ and $m'=m$ contributes, and (A11) reduces to

$$-\frac{8\pi}{kr^2}\sum_{l,m}(-i)^l\exp(2i\eta_l)\frac{\partial\eta_l}{\partial k}\exp(ikr)\sin(kr-\tfrac{1}{2}\pi l)\bar{P}_l^m(\cos\Theta_1)\bar{P}_l^m(\cos\Theta_2)\exp[im(\Phi_1-\Phi_2)]. \tag{A12}$$

Again using (A10) and (A7) gives

$$\begin{aligned}
&=-\frac{4\pi}{kr^2}\sum_l\exp(2i\eta_l)(-i)^l(2l+1)\frac{\partial\eta_l}{\partial k}\sin(kr-\tfrac{1}{2}\pi l)\exp(ikr)P_l(\cos\gamma)\\
&=\frac{2\pi i}{kr^2}\sum_l\exp(2i\eta_l)(2l+1)\frac{\partial\eta_l}{\partial k}[(-1)^l\exp(2ikr)-1]P_l(\cos\gamma)\\
&=\frac{2\pi i}{kr^2}\sum_l\exp(2i\eta_l)(2l+1)\frac{\partial\eta_l}{\partial k}(-1)^l\exp(2ikr)P_l(\cos\gamma)-\frac{2\pi i}{kr^2}\frac{\partial}{\partial k}[kf(\gamma)],
\end{aligned} \tag{A13}$$

where γ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$. Consider now the second term in (A5). Using (A6) and (A7) this may be rewritten as

$$\frac{1}{2ikr^2}\sum_{l,l'}(2l+1)(2l'+1)[\exp(-2i\eta_{l'})-1]\frac{\partial\eta_l}{\partial k}\exp(2i\eta_l)P_l(\cos\theta_2)P_{l'}(\cos\theta_1). \tag{A14}$$

Proceeding as before, using (A10) and integrating over (Θ,Φ), we obtain

$$\begin{aligned}
&\frac{4\pi}{ikr^2}\sum_{l,m}\frac{\partial\eta_l}{\partial k}[-\exp(2i\eta_l)+1]\bar{P}_l^m(\cos\Theta_1)\bar{P}_l^m(\cos\Theta_2)\exp[im(\Phi_1-\Phi_2)]\\
&=\frac{2\pi}{ikr^2}\sum_l\frac{\partial\eta_l}{\partial k}[1-\exp(2i\eta_l)]P_l(\cos\gamma)(2l+1)=-\frac{2\pi i}{kr^2}\sum_l\frac{\partial\eta_l}{\partial k}(2l+1)P_l(\cos\gamma)+\frac{2\pi i}{kr^2}\frac{\partial}{\partial k}[kf(\gamma)].
\end{aligned} \tag{A15}$$

Combining (A13) and (A15), the entire volume integration now reduces to

$$J=\frac{2\pi i}{k}\sum_l\int_R^\infty\frac{\partial\eta_l}{\partial k}(2l+1)P_l(\cos\gamma)\{\exp(2i\eta_l)(-1)^l\exp(2ikr)-1\}dr. \tag{A16}$$

Clearly this is infinite.