Virial Theorem and its Generalizations in Scattering Theory*

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Heretofore, the hypervirial theorems recently introduced by Hirschfelder have only been applied to bound-state systems. In this paper it is shown that, with certain modifications, these theorems can also be applied to free systems, and, in particular, to scattering problems. The new form of the general hypervirial theorem is derived, and the theory is illustrated with the problem of a particle scattered by a central field. The ordinary virial theorem is deduced, together with other results of physical interest. Both classical and quantum-mechanical formalisms are considered, and in some cases the semiclassical approximation links corresponding results.

I. INTRODUCTION

A WHOLE family of relations, called hypervirial theorems, which are useful both in classical and in quantum mechanics have recently been introduced by Hirschfelder.[1] The usual virial theorem is a member of this family. Some applications of these relations to bound-state systems in quantum mechanics have already been discussed.[2–4] However, as yet there has been no mention of the relevance of the hypervirial theorems to free systems, or, in particular, to scattering problems. It is the object of this paper to show that, with certain modifications, these theorems can indeed be applied to free systems.

First, we derive in a general manner the new form of the hypervirial theorem which is appropriate to a free system. Then the theory is illustrated by taking as an example the simple scattering problem of a particle under the influence of a central field. We show how the ordinary virial theorem can be deduced, together with other results of physical interest. Both classical and quantum-mechanical formalisms are considered, and the parallelism between them is emphasized. In some cases the semiclassical scattering approximation forms a bridge between corresponding results. Our techniques can be extended to more complicated scattering problems.

II. CLASSICAL HYPERVIRIAL RELATIONS

In classical mechanics, let w be any function of the generalized coordinates and momenta of a free system whose Hamiltonian is H. Then, in terms of the Poisson bracket (H,w) of H and w, we have the classical equation of motion:

$$dw/dt=(H,w). \tag{1}$$

Integrating Eq. (1) with respect to time from $t=0$ to $t=T$ along a dynamical trajectory, it follows that

$$w(T)-w(0)=\int_0^T (H,w)dt. \tag{2}$$

Here $w(t)$ denotes the value of w for the trajectory at any time t, and we suppose that $w(0)$ is not infinite.

There are now two cases to be considered. Firstly, we assume that $w(T)$ remains finite as T tends to infinity. In this case the hypervirial relation for the free system is

$$w(\infty)-w(0)=\int_0^\infty (H,w)dt. \tag{3}$$

This is different from the hypervirial relation for a bound system, which is[1]

$$0=\lim_{T\to\infty} T^{-1}[w(T)-w(0)]=\lim_{T\to\infty} T^{-1}\int_0^T (H,w)dt. \tag{4}$$

Equation (4) is actually the time average of Eq. (1). For bound states the time average of dw/dt must be zero, and meaningful results can be obtained by equating the right-hand side of (4) to zero. For free states, however, this time-averaging process does not yield any useful information. We, therefore, take (3) rather than (4) as the hypervirial relation generated by w.

Secondly, $w(T)$ might become infinite as T does. In this case, Eq. (2) must be rearranged by adding equivalent terms to each side of the equation so that each side is finite in the limit as T tends to infinity. The hypervirial relation for the free system is then obtained by taking this limit. This rearrangement of Eq. (2) is equivalent to a new choice of w; with this choice the limiting form of (2) will be like Eq. (3).

III. QUANTUM-MECHANICAL HYPERVIRIAL RELATIONS

In quantum mechanics, let W be any function of the generalized coordinates and the quantum-mechanical momentum operators of a system whose quantum-mechanical Hamiltonian is H. Then if the system is in a bound state represented by ψ, the hypervirial theorem

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[1] J. O. Hirschfelder, J. Chem. Phys. 33, 1462 (1960).
[2] S. T. Epstein and J. O. Hirschfelder, Phys. Rev. 123, 1495 (1961).
[3] J. O. Hirschfelder and C. A. Coulson, J. Chem. Phys. 36, 941 (1962).
[4] J. H. Epstein and S. T. Epstein, Am. J. Phys. 30, 266 (1962).

generated by W is[1]

$$\int \psi^*[H,W]\psi d\tau = 0. \tag{5}$$

Here $[H,W]$ is the commutator of the operators H and W; it corresponds to $-i\hbar$ times the classical Poisson bracket (H,w). The volume integration in (5) is taken throughout the region τ to which the system is confined, which could be the whole of space. This integration is a kind of space averaging, and it corresponds to the classical time averaging in Eq. (4). As an extension of (5), it is easy to show that if ψ_1 and ψ_2 are any two degenerate wave functions with the same energy, then

$$\int \psi_1[H,W]\psi_2 d\tau = 0. \tag{6}$$

If the system is not in a bound state, then the wave functions are not quadratically integrable, and relations (5) and (6) are not, in general, satisfied. To see how they must be modified, we first consider the identity

$$\int_{\tau 1} (H-E)\psi_1 W\psi_2 d\tau = \int_{\tau 1} \psi_1 W(H-E)\psi_2 d\tau. \tag{7}$$

ψ_1 and ψ_2 are now degenerate continuum wave functions with energy E, and the integration is taken through a finite region τ_1 whose boundary is a closed surface S_1. Subtracting the equal terms in E, (7) gives

$$\int_{\tau 1} (H\psi_1) W\psi_2 d\tau = \int_{\tau 1} \psi_1 W H\psi_2 d\tau. \tag{8}$$

Let us suppose that the system is the simple one of a single particle of mass m moving under a potential V; then, in atomic units,

$$H = -(2m)^{-1}\nabla^2 + V. \tag{9}$$

Assuming that $W\psi_2$ is a well-behaved function so that Green's theorem can be applied through the region τ_1, it follows that

$$\int_{\tau 1} (\nabla^2\psi_1) W\psi_2 d\tau = \int_{\tau 1} \psi_1 \nabla^2 (W\psi_2) d\tau + \int_{S_1} \{(W\psi_2)\,\mathrm{grad}\psi_1 - \psi_1\,\mathrm{grad}(W\psi_2)\}\cdot \mathbf{dS}. \tag{10}$$

It is clear that

$$\int_{\tau 1} (V\psi_1) W\psi_2 d\tau = \int_{\tau 1} \psi_1 V (W\psi_2) d\tau, \tag{11}$$

and so from (10) and (11) we have

$$\int_{\tau 1} (H\psi_1) W\psi_2 d\tau = \int_{\tau 1} \psi_1 H (W\psi_2) d\tau - (2m)^{-1}\int_{S_1} \{(W\psi_2)\,\mathrm{grad}\psi_1 - \psi_1\,\mathrm{grad}(W\psi_2)\}\cdot \mathbf{dS}. \tag{12}$$

Using the identity (8), this can be rearranged to give

$$\int_{\tau 1} \psi_1[H,W]\psi_2 d\tau = (2m)^{-1}\int_{S_1} \{(W\psi_2)\,\mathrm{grad}\psi_1 - \psi_1\,\mathrm{grad}(W\psi_2)\}\cdot \mathbf{dS}. \tag{13}$$

We now let the surface S_1 recede to infinity. If W is such that the surface integral over S_1 remains finite, then the limiting form of (13) is the hypervirial relation for a free system which corresponds to (6) for a bound system. If we set $\psi_1 = \psi^*$ and $\psi_2 = \psi$, we get the relation corresponding to (5). This is

$$\lim_{S_1\to\infty} \int_{\tau 1} \psi^*[H,W]\psi d\tau = (2m)^{-1} \lim \int_{S_1} \{(W\psi)\,\mathrm{grad}\psi^* - \psi^*\,\mathrm{grad}(W\psi)\}\cdot \mathbf{dS}. \tag{14}$$

The proof of (5) and (6) for a single particle in a bound state is actually implicit in the relations (13) and (14). As S_1 recedes to infinity, then provided W is sufficiently well behaved, bound-state wave functions tend to zero sufficiently fast to ensure the vanishing of the surface integrals. It should be noted that (13) and (14) can readily be generalized if the system consists not of one but of n particles, with masses m_i, $i=1, 2, \cdots, n$. The Hamiltonian is then

$$H = -\sum_i (2m_i)^{-1}\nabla_i^2 + V, \tag{15}$$

and $m^{-1}\,\mathrm{grad}$ in (13) and (14) is replaced by $\sum_i m_i^{-1}\,\mathrm{grad}_i$.

Sometimes it is necessary to modify the choice of W so that the integrals in (13) and (14) do remain finite in the limit. This is analogous to an adjustment of the classical w. In addition, it can be convenient to consider the commutator $[H-E, W]$ rather than $[H,W]$ in Eqs. (13) and (14). The results with this commutator may be different if W is a function of E. They arise naturally if the E is retained in Eq. (7); no changes are necessary on the right-hand sides of (13) and (14).

IV. THE CLASSICAL SCATTERING OF A PARTICLE BY A CENTRAL FIELD

We consider the motion of a particle which approaches some origin O from infinity, and is under the sole influence of a field centered at O (see Fig. 1). We denote the various properties of the particle and its trajectory as follows: m = the mass, k = the linear momentum at infinity, b = the impact parameter, r = the distance from O, r_0 = the distance of closest approach to O, $V(r)$ = the potential energy, $p=m\dot{r}$ = the radial momentum, θ = the decreasing angle between the radius vector and the original direction of the trajectory, χ = the scattering angle (that between the original and terminal directions). The time $t=0$ is taken when $r=r_0$ and $p=0$; thus the motion extends from $t=-\infty$ to $t=+\infty$. The angular momentum of the particle about O is constant, and so

$$-mr^2\dot{\theta}=bk. \tag{16}$$

The classical Hamiltonian H of the particle is given by

$$H=(2m)^{-1}(p^2+b^2k^2/r^2)+V(r), \tag{17}$$

and, because the energy of the particle is conserved, we have

$$H=k^2/2m=\text{const.} \tag{18}$$

It is convenient to know the asymptotic behavior of r when t is large. From (17) and (18) we see that, for $t\geq 0$,

$$p=m\dot{r}=k(1-2mV/k^2-b^2/r^2)^{1/2}. \tag{19}$$

We make the assumption that, as r tends to infinity,

$$V(r)\sim r^{-\alpha},\quad \text{where}\quad \alpha>1. \tag{20}$$

It follows from (19) that, when t and r are large, $p\sim k$ and

$$r\sim s+kt/m. \tag{21}$$

The quantity s in (21) appears as a constant of integration; it is an important property of the trajectory which is useful in kinetic theory. With a Coulomb potential $V=\lambda/r$, (21) is replaced by

$$r+(m\lambda/k^2)\ln r\sim s+kt/m. \tag{22}$$

A. The Virial Theorem

For bound trajectories, the ordinary virial theorem is generated by $w=rp$; however, for a scattering process, rp becomes infinite as t does. To obtain the appropriate form of the virial theorem here, we choose

$$w=r(p-k). \tag{23}$$

Using (17), (19), and (23), we have

$$(H,w)\equiv\frac{\partial H}{\partial p}\frac{\partial w}{\partial r}-\frac{\partial H}{\partial r}\frac{\partial w}{\partial p}=\frac{k}{m}(k-p)-\left(2V+r\frac{dV}{dr}\right). \tag{24}$$

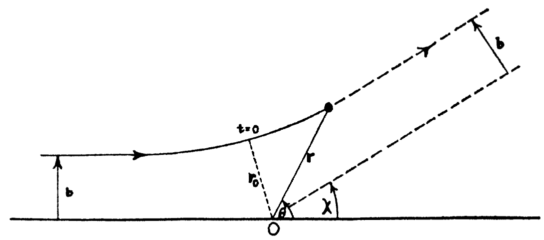

FIG. 1. Classical trajectory.

Equation (2) now gives

$$\Big[r(p-k)\Big]_{t=0}^{T}=k^2T/m-k\Big[r\Big]_{t=0}^{T}-\int_{t=0}^{T}\left(2V+r\frac{dV}{dr}\right)dt. \tag{25}$$

From (19) and (20), we can see that $r(p-k)$ tends to zero as T tends to infinity. Thus, proceeding to the limit in (25), and making use of (21), we get for the virial theorem:

$$\int_{t=0}^{\infty}\left(2V+r\frac{dV}{dr}\right)dt=-ks. \tag{26}$$

This result (26) has been obtained by Demkov,[5] who takes as his starting point a modified form of Hamilton's principle. It can also be verified directly from Eq. (19), without reference to a virial, but it is not an obvious result to derive *ab initio*. The result does not hold for a Coulomb potential; it is evident from (22) that the right-hand side of Eq. (25) would then become infinite in the limit.

B. Hypervirial Relations

Various hypervirial relations are generated by taking, for example,

$$w=f(r)p, \tag{27}$$

where $f(r)$ is such that $w\to 0$ as $t\to\infty$. It can be shown that

$$(H,w)=(k^2/m)[(1-b^2/r^2)df/dr+b^2f/r^3]-(2Vdf/dr+fdV/dr). \tag{28}$$

Here w is zero both when $t=0$ and when $t=\infty$; thus from (3) the hypervirial relations are given by equating to zero the integral from $t=0$ to $t=\infty$ of expression (28).

The choice $f(r)=r^{-1}$ leads to

$$0=-\left(\frac{k^2}{m}\right)\int_0^{\infty}r^{-2}dt+\int_0^{\infty}\left(\frac{2k^2b^2}{mr^4}+2r^{-2}V-r^{-1}\frac{dV}{dr}\right)dt. \tag{29}$$

[5] Y. N. Demkov, Doklady Akad. Nauk S.S.S.R. **138**, 86 (1961) [translation: Soviet Phys.—Doklady **6**, 393 (1961)].

From Eq. (16) and Fig. 1 we see that

$$\int_0^\infty r^{-2}dt=-\left(\frac{m}{bk}\right)\int_{t=0}^\infty d\theta=(\pi-\chi)\frac{m}{2bk}. \tag{30}$$

Combining (29) and (30), we obtain a new expression for the scattering angle χ, viz.,

$$\pi-\chi=\left(\frac{2b}{k}\right)\int_0^\infty\left(\frac{2k^2b^2}{mr^4}+2r^{-2}V-r^{-1}\frac{dV}{dr}\right)dt. \tag{31}$$

The more usual expression for χ,

$$\pi-\chi=2b\int_{t_0}^\infty r^{-2}\left(1-\frac{2mV}{k^2}-\frac{b^2}{r^2}\right)^{1/2}dr \tag{32}$$

[which follows directly from (19) and (30)], can be recovered from (31) with the help of an integration by parts.

If we choose $f(r)=r^{-n}$ in (27), then the hypervirial relation which follows from (3) gives a reduction formula for the integral $I_n=\int_{t=0}^\infty r^{-n}dt$. This is, for $n\geq 1$,

$$b^2(n+1)I_{n+3}=nI_{n+1}-mk^{-2}\int_0^\infty\left(2nr^{-n-1}V-r^{-n}\frac{dV}{dr}\right)dt. \tag{33}$$

Equation (33) is also true for a Coulomb potential, when it would lead to a recurrence relation connecting I_{n+1}, I_{n+2}, and I_{n+3}.

V. THE QUANTUM-MECHANICAL SCATTERING OF A PARTICLE BY A CENTRAL FIELD

We use the notation of the previous section, and work in atomic units with $\hbar=1$. The wave equation is

$$\nabla^2\psi+(k^2-2mV)\psi=0, \tag{34}$$

for which is required a solution with asymptotic form[6]

$$\psi\sim\exp(i\mathbf{k}\cdot\mathbf{r})+r^{-1}\exp(ikr)F(\theta) \tag{35}$$

for large r. Here $\mathbf{k}$ is the linear momentum vector of the particle before it is affected by the potential $V(r)$, and $\mathbf{r}$ is the position vector of the particle. If $\psi_1(\mathbf{k}_1,\theta_1)$ and $\psi_2(\mathbf{k}_2,\theta_2)$ are two solutions of (34) representing particles with the same energy $E=k^2/2m$, but with different initial directions, then according to the discussion in Sec. III the general hypervirial relation is the limiting form of

$$\int\psi_1\left[H-\frac{k^2}{2m},W\psi_2\right]d\tau=(2m)^{-1}\int[(W\psi_2)\,\mathrm{grad}\psi_1-\psi_1\,\mathrm{grad}(W\psi_2)]\cdot\mathbf{dS}. \tag{36}$$

[6] See, for example, N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1949), 2nd ed.

H is now the quantum-mechanical Hamiltonian, given in (9).

It is frequently convenient to decompose a solution ψ of (34) into partial waves $\phi_n(r)$ by the substitution

$$\psi=\sum_{n=0}^\infty A_nP_n(\cos\theta)r^{-1}\phi_n(r). \tag{37}$$

Here $\phi_n(r)$ is the (real) solution of the equation[6]

$$d^2\phi_n/dr^2+[k^2-2mV-n(n+1)/r^2]\phi_n=0, \tag{38}$$

which is zero at the origin and has the asymptotic form

$$\phi_n(r)\sim k^{-1}\sin(kr-\tfrac{1}{2}n\pi+\eta_n) \tag{39}$$

for large r. The coefficients in the expansion (37) are given by the formula

$$A_n=(2n+1)i^n\exp(i\eta_n). \tag{40}$$

In order that the phases η_n should be finite, it is necessary to make the assumption (20) about $V(r)$. Equation (38) is a one-dimensional Schrödinger-type equation for a wave function ϕ_n, with the effective Hamiltonian

$$H_0=-(2m)^{-1}d^2/dr^2+V(r)+n(n+1)/2mr^2. \tag{41}$$

It is easy to show, using integration by parts, that the hypervirial theorem for the partial wave ϕ_n is

$$\int_{r=0}^\infty\phi_n\left[H_0-\frac{k^2}{2m},W\right]\phi_n dr=(2m)^{-1}\left[(W\phi_n)\frac{d\phi_n}{dr}-\phi_n\frac{d}{dr}(W\phi_n)\right]_{r=0}^\infty. \tag{42}$$

A. The Virial Theorem

Corresponding to the classical w of (23), the quantum-mechanical virial theorem is generated by

$$W=\mathbf{r}\cdot\mathrm{grad}-kd/dk=rd/dr-kd/dk. \tag{43}$$

With this choice for W, it follows that

$$[H-k^2/2m,W]\psi=-[m^{-1}(\nabla^2+k^2)+rdV/dr]\psi=-(2V+rdV/dr)\psi, \tag{44}$$

and

$$[H_0-k^2/2m,W]\phi_n=-\{m^{-1}(d^2/dr^2+k^2)+rd/dr[V+n(n+1)/2mr^2]\}\phi_n=-(2V+rdV/dr)\phi_n. \tag{45}$$

Using (35), we can also show that, for large r:

$$(W\psi_2)\frac{d\psi_1}{dr}-\psi_1\frac{d}{dr}(W\psi_2)=[ik(1-\cos\theta_1)r^{-1}-r^{-2}]\times\exp[ikr(1+\cos\theta_1)]\frac{d}{dk}[kF(\theta_2)]+O(r^{-\beta}). \tag{46}$$

Here $\beta>2$ provided that we again make the assumption

(20). From (37), (38), and (39) this assumption implies that the correction to ψ in (35) is $O(r^{-\beta})$, where $\beta>2$, and this latter property is needed in deriving (46).

Let us take the surface S in (36) to be a sphere with center O and radius R. The only contribution to the surface integral which does not vanish in the limit as R tends to infinity is, from (46),

$$2\pi(2m)^{-1}\int_{\theta_1=0}^{\pi}(1-\cos\theta_1)\frac{d}{dk}[kF(\theta_2)] \times\exp[ikR(1+\cos\theta_1)]Rik\sin\theta_1 d\theta_1. \quad (47)$$

Integrating by parts, (47) yields

$$\left(\frac{\pi}{m}\right)\left[-(1-\cos\theta_1)\frac{d}{dk}[kF(\theta_2)] \times\exp[ikR(1+\cos\theta_1)]\right]_{\theta_1=0}^{\pi}+O(R^{-1}) =-\left(\frac{2\pi}{m}\right)\frac{d}{dk}[kF(\pi-\gamma)]+O(R^{-1}), \quad (48)$$

where γ is the angle between the directions of $\mathbf{k}_1$ and $\mathbf{k}_2$. Thus from (36), (44), and (48) the virial theorem for complete wave functions is

$$\int\psi_1\left(2V+r\frac{dV}{dr}\right)\psi_2 d\tau=\left(\frac{2\pi}{m}\right)\frac{d}{dk}[kF(\pi-\gamma)]. \quad (49)$$

For the partial wave ϕ_n, the right-hand side of (42) becomes, using (39) and (43), precisely $-(2m)^{-1}d\eta_n/dk$. Hence from (42) and (45) the virial theorem for ϕ_n is

$$\int_{r=0}^{\infty}\phi_n\left(2V+r\frac{dV}{dr}\right)\phi_n dr=(2m)^{-1}\frac{d\eta_n}{dk}. \quad (50)$$

It is possible to check the consistency of the results (49) and (50) in the case when $\psi_1=\psi_2=\psi$ with the help of the expansion (37) and formula (40).

Demkov[7] has derived the virial theorems (49) and (50) starting with Hulthén's variational principle, but our methods seem more straightforward and better illustrate the parallelism between the classical and quantum-mechanical formalisms.

As Demkov[5] points out, the correspondence between (50) and the classical result (26) may be demonstrated with the help of the semiclassical scattering approximation.[6] We define

$$F(r)=k^2-2mV-(n+\tfrac{1}{2})^2/r^2, \quad (51)$$

and assume that $F(r)$ has just one simple zero at $r=r_0$. This corresponds to the classical case, where $F^{1/2}$ is replaced by $m\dot{r}$ and $(n+\frac{1}{2})$ is replaced by bk [see Eq. (19)]. According to the WKB approximation which is employed,[8] it can be shown that

$$\phi_n=k^{-1/2}F^{-1/4}\sin\left(\tfrac{1}{4}\pi+\int_{r_0}^{r}F^{1/2}dr\right),\quad r>r_0;$$
$$\phi_n=\tfrac{1}{2}k^{-1/2}|F|^{-1/4}\exp\left(-\int_{r}^{r_0}|F|^{1/2}dr\right),\quad r<r_0. \quad (52)$$

From the form of (52) when r is large, it follows that the phase is

$$\eta_n=\tfrac{1}{4}\pi+\tfrac{1}{2}n\pi-kr_0+\int_{r_0}^{\infty}(F^{1/2}-k)dr, \quad (53)$$

which yields

$$\frac{d\eta_n}{dk}=-r_0+\int_{r_0}^{\infty}(kF^{-1/2}-1)dr. \quad (54)$$

The semiclassical approximation is only valid for large phases; thus in an integral over r it is reasonable to replace the rapidly oscillating ϕ_n by its root-mean-square value when $r>r_0$, and the exponentially decreasing ϕ_n by zero when $r<r_0$. When this is done, (50) becomes

$$(2k)^{-1}\int_{r=r_0}^{\infty}F^{-1/2}\left(2V+r\frac{dV}{dr}\right)dr=(2m)^{-1}\frac{d\eta_n}{dk}. \quad (55)$$

Finally, if $F^{1/2}$ is replaced by the classical $m\dot{r}$, then using (21) Eq. (54) gives

$$d\eta_n/dk=-s, \quad (56)$$

and (55) becomes identical with the classical virial theorem (26).

B. Hypervirial Relations

It is not as easy as it seems at first sight to extract useful results for quantum-mechanical scattering from the formal hypervirial theorems (36) and (42). The problem is to select a W for which the integrals converge, and which gives a finite or zero expression on the right-hand side of (42). Powers of $(rd/dr-kd/dr)$ for W give results which, though interesting, can be derived from (49) or (50). The choice $re^{-\alpha r}d/dr$ leads to a relation which follows from the Laplace transform of Eq. (38).

One apparently new result is generated from (42) by the simple choice $W=d/dn$. We have

$$[H_0-k^2/2m,\, d/dn]=-(2n+1)/2mr^2, \quad (57)$$

and, using (39), the contribution to the right-hand side of (42) at $r=\infty$ is $(d\eta_n/dn-\frac{1}{2}\pi)/2mk$. At $r=0$, there is no contribution if we assume that V does not have a singularity worse than r^{-t}, where[9] $t<2$, for then it follows that

$$\phi_n\sim k^{-1}r^{n+1}\quad\text{for small } r. \quad (58)$$

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

[8] R. E. Langer, Phys. Rev. **51**, 669, 1937.

[9] Even if $t=2$, there is still no contribution at $r=0$ for a repulsive field.

Thus, we arrive at the equation

$$(2n+1)\int_0^\infty \frac{\phi_n^2}{r^2}dr = k^{-1}\left(\tfrac{1}{2}\pi - \frac{d\eta_n}{dn}\right). \quad (59)$$

In the semiclassical approximation, the techniques described in (A) above may be used to show that (59) becomes the more familiar result[6]

$$\tfrac{1}{2}\chi = d\eta_n/dn. \quad (60)$$

If some restriction is placed on n, the relation (58) may well imply the convergence of certain integrals at the origin, and so widen the field of choice for W. For example, with $W=r^{-1}d/dr$, we have

$$[H_0-k^2/2m, r^{-1}d/dr]\phi_n = [-k^2r^{-2}+2n(n+1)r^{-4}-r^{-3}d/dr+2mr^{-2}V - mr^{-1}dV/dr]m^{-1}\phi_n. \quad (61)$$

Assuming that $n\geq 1$ (i.e., ruling out the s wave ϕ_0), there is no contribution to the right-hand side of (42). Integrating the $d\phi_n/dr$ term by parts, we obtain from (42) and (61)

$$-k^2m^{-1}\int_0^\infty \frac{\phi_n^2}{r^2}dr + (2n^2+2n-\tfrac{3}{2})m^{-1}\int_0^\infty \frac{\phi_n^2}{r^4}dr + \int_0^\infty \phi_n^2\left(2r^{-2}V - r^{-1}\frac{dV}{dr}\right)dr = 0. \quad (62)$$

The relation (58) ensures the convergence of the integrals, provided that $n\geq 1$. Equation (62) is the quantum-mechanical analog of (29), and becomes identical with it in the semiclassical approximation when n is large. Equations (59) and (62) can be combined to give an alternative expression for $d\eta_n/dn$.

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Hypervirial Theorems for Variational Wave Functions in Scattering Theory*

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The form of hypervirial theorem which is appropriate in scattering theory is discussed in general terms. It is shown that variational wave functions which are optimized in accordance with Kohn's variational principle do satisfy hypervirial theorems. Thus such theorems may be useful in selecting approximate wave functions to give accurate phase shifts or scattering amplitudes. The situation is analogous to that of energy-optimized wave functions for bound-state systems.

I. INTRODUCTION

As Epstein and Hirschfelder have shown,[1] if an approximate bound-state wave function ψ_t admits a variation $\delta\psi_t$ such that

$$\delta\psi_t = i\epsilon W\psi_t, \quad (1)$$

where W is a Hermitian operator, then the corresponding variation δE_t in the energy E_t of the state is given by

$$(\psi_t,\psi_t)\delta E_t = (\delta\psi_t, \{H-E_t\}\psi_t) + (\psi_t, \{H-E_t\}\delta\psi_t) = i\epsilon(\psi_t,[H,W]\psi_t). \quad (2)$$

This result follows immediately from the Hermitian property of W. Thus, if ψ_t is selected to satisfy the hypervirial theorem for a bound state

$$(\psi_t,[H,W]\psi_t)=0, \quad (3)$$

then, as far as variations of the form (1) are concerned, ψ_t is automatically optimized to give the best energy E_t.

In this paper we show that an analogous situation exists for approximate wave functions in scattering theory, provided that the form of the hypervirial theorem is employed which is appropriate to a free system. We find that if Kohn's variational principle[2] for phase shifts is used to optimize a partial wave, then this partial wave satisfies a hypervirial theorem. For total wave functions, a form of Kohn's principle for scattering amplitudes again leads to such a theorem. Thus hypervirial theorems may be helpful in selecting approximate wave functions in scattering theory, as they are with bound-state systems.

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