Thus, we arrive at the equation

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

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

$$\tfrac{1}{2}\chi = d\eta_n/dn. \tag{60}$$

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

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

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)

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

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

$$\delta\psi_t = i\epsilon W\psi_t, \tag{1}$$

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

$$\begin{aligned}(\psi_t,\psi_t)\delta E_t &= (\delta\psi_t, \{H-E_t\}\psi_t) + (\psi_t, \{H-E_t\}\delta\psi_t) \\ &= i\epsilon(\psi_t,[H,W]\psi_t).\end{aligned} \tag{2}$$

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

$$(\psi_t,[H,W]\psi_t)=0, \tag{3}$$

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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[1] S. T. Epstein and J. O. Hirschfelder, Phys. Rev. **123**, 1495 (1961).
[2] W. Kohn, Phys. Rev. **74**, 1763 (1948).

The modifications to the hypervirial relations which are necessary for free systems were discussed in the preceding paper,[3] but we briefly recapitulate here; the bracket notation is retained for generality and conciseness. For an exact bound-state wave function ψ, the hypervirial theorem

$$(\psi,[H,W]\psi)=0 \tag{4}$$

is a consequence of the Hermitian property of H, i.e.,

$$(\psi,HW\psi)-(H\psi,W\psi)=0,$$

and of Schrödinger's equation. With continuum wave functions, however, the quantity

$$\Sigma\equiv(\psi,HW\psi)-(H\psi,W\psi) \tag{6}$$

is not, in general, zero because ψ does not now tend to zero at large distances. Σ is a surface integral, or, for a one-dimensional system, merely the difference of end-point values. Meaningful hypervirial relations arise when Σ is finite, or possibly even when it is zero because of the nature of W. When Σ is not zero, we say that H is "nominally Hermitian." We have

$$\begin{aligned}(\psi,[H,W]\psi)&\equiv(\psi,HW\psi)-(\psi,WH\psi)\\&=\Sigma+(H\psi,W\psi)-(\psi,WH\psi),\end{aligned} \tag{7}$$

and because $H\psi=E\psi$ the last two terms in (7) cancel each other to give the more general form of the hypervirial theorem:

$$(\psi,[H,W]\psi)=\Sigma. \tag{8}$$

With degenerate wave functions ψ_1 and ψ_2, we should have, in obvious notation:

$$(\psi_1,[H,W]\psi_2)=\Sigma_{12}. \tag{9}$$

In the preceding paper,[3] particular cases of (8) and (9) were utilized which are relevant for the scattering of a particle of mass m by a central field. For the (real) partial wave ϕ corresponding to the effective Hamiltonian

$$H_0=-(2m)^{-1}d^2/dr^2+V(r)+n(n+1)/2mr^2, \tag{10}$$

relation (8) gives

$$\int_{r=0}^{\infty}\phi[H_0,W]\phi dr =(2m)^{-1}[(W\phi)d\phi/dr-\phi(d/dr)(W\phi)]_{r=0}^{\infty}. \tag{11}$$

Relation (9) yields, for any two degenerate total wave functions,

$$\int\psi_1{}^*[H,W]\psi_2d\tau=(2m)^{-1}\int\{W\psi_2\,\mathrm{grad}\psi_1{}^* -\psi_1{}^*\,\mathrm{grad}(W\psi_2)\}\cdot\mathbf{dS}; \tag{12}$$

here the surface integral extends over the surface enclosing the volume τ, which in the limit includes the whole of space.

II. HYPERVIRIAL THEOREMS FOR APPROXIMATE PARTIAL WAVES

The exact partial wave $\phi(r)$ is frequently defined as the solution of the equation

$$H_0\phi=E\phi \quad (\text{where } E=k^2/2m), \tag{13}$$

with the boundary conditions

$$\phi(0)=0, \tag{14}$$

and

$$\phi(r)\sim k^{-1}\sin(kr-\tfrac{1}{2}n\pi+\eta) \quad \text{for large } r. \tag{15}$$

Without loss of generality, we absorb the factor $\cos\eta$ into ϕ and take instead of (15):

$$\phi(r)\sim k^{-1}\sin(kr-\tfrac{1}{2}n\pi)+\lambda\cos(kr-\tfrac{1}{2}n\pi), \tag{16}$$

where

$$\lambda=k^{-1}\tan\eta. \tag{17}$$

Suppose now an approximate trial partial wave $\phi_t(r)$ satisfies the boundary conditions

$$\phi_t(0)=0, \tag{18}$$

and

$$\phi_t(r)\sim k^{-1}\sin(kr-\tfrac{1}{2}n\pi)+\lambda_t\cos(kr-\tfrac{1}{2}n\pi) \quad \text{for large } r. \tag{19}$$

Then Kohn's variational principle[2] states that the optimum ϕ_t is determined by

$$(2m)^{-1}\delta\lambda_t+\delta\int_0^\infty\phi_t(E-H_0)\phi_t dr=0. \tag{20}$$

We will prove that if the variation in ϕ_t is such that

$$\delta\phi_t=i\epsilon W\phi_t, \tag{21}$$

where W is a nominally Hermitian operator, then the optimum trial function ϕ_t derived from Kohn's principle satisfies the hypervirial theorem

$$(\phi_t,[H_0,W]\phi_t)=\Sigma_{tt}. \tag{22}$$

Kohn's principle for partial waves follows from the following equation, which holds for variations of ϕ_t about the exact function ϕ:

$$\int_0^\infty\phi_t(E-H_0)\phi_t dr+(\lambda_t-\lambda)/2m =\int_0^\infty\phi(E-H_0)\phi dr=0. \tag{23}$$

Equation (23) is obtained by integrating by parts, and neglecting the second-order term in $(\phi_t-\phi)$.

[3] P. D. Robinson and J. O. Hirschfelder, preceding paper [Phys. Rev. 129, 1391 (1963)].

From Eq. (20) it follows that

$$(2m)^{-1}\delta\lambda_t+(\delta\phi_t,\{E-H_0\}\phi_t)+(\phi_t,\{E-H_0\}\delta\phi_t)=0. \quad (24)$$

We also need the exact result

$$(2m)^{-1}\delta\lambda_t+(H_0\phi_t,\delta\phi_t)-(\phi_t,H_0\delta\phi_t)=0; \quad (25)$$

this is established with the help of a partial integration similar to that required for (23), and depends on the boundary conditions (18) and (19). Expanding (24), and substituting from (21), we get

$$(2mi\epsilon)^{-1}\delta\lambda_t-E(W\phi_t,\phi_t)+E(\phi_t,W\phi_t)$$
$$+(W\phi_t,H_0\phi_t)-(\phi_t,H_0W\phi_t)=0. \quad (26)$$

Now, by hypothesis, W is a nominally Hermitian operator; thus the difference of $(W\phi_t,H_0\phi_t)$ and $(\phi_t,WH_0\phi_t)$ is, in general, a surface integral, which in this one-dimensional case reduces to a difference of end-point values. The boundary conditions (18) and (19) imposed upon ϕ_t, together with the fact that $H_0\phi_t\sim E\phi_t$ when r is large, imply that this same "surface" term is also given by the difference of $(W\phi_t,E\phi_t)$ and $(\phi_t,WE\phi_t)$. It follows that

$$(W\phi_t,H_0\phi_t)-(\phi_t,WH_0\phi_t)$$
$$=E(W\phi_t,\phi_t)-E(\phi_t,W\phi_t). \quad (27)$$

Making use of (27), Eq. (26) becomes

$$(2mi\epsilon)^{-1}\delta\lambda_t=(\phi_t,[H_0,W]\phi_t). \quad (28)$$

If we substitute for $\delta\phi_t$ from (21) into Eq. (25), we obtain also

$$(2mi\epsilon)^{-1}\delta\lambda_t=(\phi_t,H_0W\phi_t)-(H_0\phi_t,W\phi_t)\equiv\Sigma_{tt}. \quad (29)$$

Thus, from (28) and (29), the hypervirial theorem (22) is satisfied.

We can trace the argument in reverse, and so the hypervirial theorem is really equivalent to Kohn's principle. The principle has been shown[4] to be a minimum principle in many situations, and so hypervirial theorems may serve as helpful criteria in selecting approximate partial waves to give accurate phase shifts. It should be noted, however, that the boundary conditions (18) and (19) imply a restriction on $\delta\phi_t$ and, hence, on W. In particular, a simple scale transformation is not allowed.

[4] L. Rosenberg and L. Spruch, Phys. Rev. **125**, 1407 (1962), and references given therein.

III. HYPERVIRIAL THEOREMS FOR APPROXIMATE TOTAL WAVE FUNCTIONS

The ideas of Sec. II can readily be extended to include approximate total wave functions. The exact wave function ψ_j representing a particle with incident momentum $\mathbf{k}_j$ is the solution of

$$H\psi=[-(2m)^{-1}\nabla^2+V(r)]\psi=E\psi, \quad (30)$$

which is finite at the origin and has the asymptotic form

$$\psi_j\sim\exp(i\mathbf{k}_j\cdot\mathbf{r})+F(\theta_j)r^{-1}\exp(ikr) \text{ for large } r \quad (31)$$

Here $|\mathbf{k}_j|=k$, θ_j is the angle between $\mathbf{k}_j$ and $\mathbf{r}$, and $F(\theta_j)$ is the scattering amplitude upon which scattering cross sections directly depend. Let ψ_{1t} and ψ_{2t} be two approximate wave functions, which satisfy the correct boundary conditions but have approximate scattering amplitudes $F_t(\theta_1)$ and $F_t(\theta_2)$. An appropriate form of Kohn's variational principle is now[2]

$$(2\pi/m)\delta F_t(\gamma)+\delta\int\psi_{1t}^*(E-H)\psi_{2t}d\tau=0, \quad (32)$$

where γ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$. This gives, in bracket notation,

$$(2\pi/m)\delta F_t(\gamma)+(\delta\psi_{1t},\{E-H\}\psi_{2t})$$
$$+(\psi_{1t},\{E-H\}\delta\psi_{2t})=0. \quad (33)$$

We also have the result, which follows from Green's theorem, that

$$(2\pi/m)\delta F_t(\gamma)+(H\psi_{1t},\delta\psi_{2t})-(\psi_{1t},H\delta\psi_{2t})=0. \quad (34)$$

Now if we assume that

$$\delta\psi_{jt}=i\epsilon W\psi_{jt}, \quad j=1,2, \quad (35)$$

then using the technique of Sec. II it is easy to show that Eqs. (33) and (34) become, respectively,

$$(2\pi/mi\epsilon)\delta F_t(\gamma)=(\psi_{1t},[H,W]\psi_{2t}), \quad (36)$$

and

$$(2\pi/mi\epsilon)\delta F_t(\gamma)$$
$$=(\psi_{1t},HW\psi_{2t})-(H\psi_{1t},W\psi_{2t})\equiv\Sigma_{1t,2t}. \quad (37)$$

Thus, from (36) and (37), we see that the hypervirial theorem

$$(\psi_{1t},[H,W]\psi_{2t})=\Sigma_{1t.2t} \quad (38)$$

is satisfied, and is again equivalent to the appropriate form of Kohn's variational principle.