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**THEORETICAL CHEMISTRY INSTITUTE
THE UNIVERSITY OF WISCONSIN**

**A STUDY OF ONE AND TWO ELECTRON CENTRAL FORCE
PROBLEMS USING THE HYPERVIRIAL THEOREM**

by

Sidney L. Gordon

WIS-TCI-8

Series 3

10 January 1963

MADISON, WISCONSIN

CATALOGUE OF ASIA
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296035

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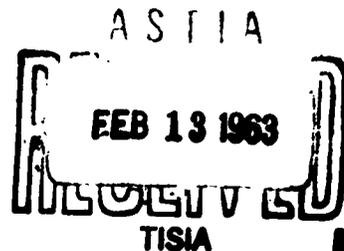
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ABSTRACT

△ The hypervirial theorem is used to develop expectation value relationships for one and two electron central force problems.

Ground state helium trial functions are scaled to identically satisfy a particular family of these relationships. It is shown that this procedure results in improved expectation values for positive powers of the radial coordinate.

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* 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.

** National Science Foundation Post-Doctoral Fellow.

A STUDY OF ONE AND TWO ELECTRON CENTRAL FORCE PROBLEMS
USING THE HYPERVIRIAL THEOREM

Sidney L. Gordon

The hypervirial theorem¹ states that

$$(\Psi, [H, W]\Psi) = 0 \quad (1)$$

Here, H is the Hamiltonian operator.

Ψ is a bound state eigenfunction of H .

W is called a hypervirial operator, and is a time independent function of the coordinates and conjugate momenta. W must be chosen so that H is hermitian with respect to Ψ and $W\Psi$, e.g.

$$(\Psi, HW\Psi) = (H\Psi, W\Psi). \quad (2)$$

The square brackets represent the commutator of H and W , defined by $[H, W] = HW - WH$.

Epstein and Epstein² used (1) to develop expectation value relationships for the non-relativistic and relativistic hydrogen atom, and for the isotropic harmonic oscillator. We extend their procedure to the non-relativistic one and two electron central force problems in sections I and II of this paper, and develop a variety of hypervirial relations. In section III, we scale approximate ground state helium wave functions to satisfy a particular family of these relations.

I. One Electron Central Force Problem

The Hamiltonian for a one electron central force problem is

$$H = \frac{p^2}{2m} + \frac{k^2}{2mr^2} + V(r) \quad (3)$$

where r is the radial coordinate of the electron.

p is the momentum conjugate to r , and is explicitly given by

the expression³ $p = -i\hbar \frac{1}{r} \frac{\partial}{\partial r} (r \quad)$.

k^2 is the square of the orbital angular momentum, and for this problem is a number equal to $l(l+1)\hbar^2$.

V is the central force potential energy and is a function of r only.

Let us consider as the hypervirial operator

$$W = f p \quad (4)$$

where f is a function of r . Using the commutator relations

$$[AB, C] = A[B, C] + [A, C]B \quad (5)$$

and

$$[p, f] = -i\hbar \frac{\partial f}{\partial r}, \quad (6)$$

we find that

$$\begin{aligned} \langle [H, fp] \rangle &= -\frac{i\hbar}{m} \langle \frac{\partial f}{\partial r} p^2 \rangle - \frac{\hbar^2}{2m} \langle \frac{\partial^2 f}{\partial r^2} p \rangle \\ &\quad - i\hbar \frac{k^2}{m} \langle f r^{-3} \rangle + i\hbar \langle f \frac{\partial V}{\partial r} \rangle \\ &= 0 \end{aligned} \quad (7)$$

where the angular brackets stand for the expectation value using a bound state eigenfunction. The expression (7) is zero because of the hypervirial theorem. Now,

$$\langle [H, \frac{\partial f}{\partial r}] \rangle = 0. \quad (8)$$

Expanding equation (8) we find that

$$\langle \frac{\partial^2 f}{\partial r^2} p \rangle = \frac{i\hbar}{2} \langle \frac{\partial^3 f}{\partial r^3} \rangle. \quad (9)$$

Multiplying eq. (3) on the left by $\frac{\partial f}{\partial r}$ and taking the expectation value, we deduce that

$$\frac{1}{2m} \left\langle \frac{\partial f}{\partial r} p^2 \right\rangle = E \left\langle \frac{\partial f}{\partial r} \right\rangle - \frac{\hbar^2}{2m} \left\langle r^{-2} \frac{\partial f}{\partial r} \right\rangle - \left\langle \sqrt{V} \frac{\partial f}{\partial r} \right\rangle. \quad (10)$$

Substituting (9) and (10) into (7), and rearranging terms we find that

$$E \left\langle \frac{\partial f}{\partial r} \right\rangle - \frac{\hbar^2}{2m} \left(\left\langle r^{-2} \frac{\partial f}{\partial r} \right\rangle - \left\langle f r^{-3} \right\rangle \right) + \frac{\hbar^2}{2m} \left\langle \frac{\partial^3 f}{\partial r^3} \right\rangle = \left\langle \sqrt{V} \frac{\partial f}{\partial r} \right\rangle + \frac{1}{2} \left\langle f \frac{\partial V}{\partial r} \right\rangle. \quad (11)$$

We now specialize (11) by letting

$$f = r^n \quad (12)$$

where n is an integer. We show in the appendix that condition (2) is satisfied when

$$n \geq 1 - 2l \quad (13)$$

where l is the angular momentum quantum number of the state. Then, after rearranging,

$$n E \left\langle r^{n-1} \right\rangle + \frac{(n-1)}{2m} \left[\frac{\hbar^2 n(n-2)}{4} - \hbar^2 \right] \left\langle r^{n-3} \right\rangle = n \left\langle \sqrt{V} r^{n-1} \right\rangle + \frac{1}{2} \left\langle r^n \frac{\partial V}{\partial r} \right\rangle. \quad (14)$$

Equation (14) shows how the expectation values of the powers of r are influenced by the type of central potential. If we let $V = -e^2 r^{-1}$ and $V = \frac{1}{2} m \omega^2 r^2$ we obtain Epstein's relations² for the nonrelativistic hydrogen atom and isotropic harmonic oscillator, respectively.

II. Two Electron Central Force Problem

The Hamiltonian for the two electron central force problem is given by

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + \frac{k_1^2}{2mr_1^2} + \frac{k_2^2}{2mr_2^2} + V_1 + V_2 + V_{12} \quad (15)$$

where r_1 is the radial coordinate of electron 1.

r_2 is the radial coordinate of electron 2.

p_1 is the momentum conjugate to r_1 .

p_2 is the momentum conjugate to r_2 .

$k_1^2 = -\hbar^2 \left(\frac{1}{\sin\theta_1} \frac{\partial}{\partial\theta_1} \sin\theta_1 \frac{\partial}{\partial\theta_1} + \frac{1}{\sin^2\theta_1} \frac{\partial^2}{\partial\theta_1^2} \right)$
with a similar expression for k_2^2 .

V_1 is a function of r_1 .

V_2 is a function of r_2 .

V_{12} is a function of r_{12} , the distance between electrons 1 and 2. Because of the V_{12} term, k_1^2 and k_2^2 are not numbers.

As the hypervirial operator, consider

$$W = f p_1 \quad (16)$$

where f is a function of r_1 and r_2 . Corresponding to equation (7), we obtain

$$\begin{aligned} \langle [H, W] \rangle &= \frac{i\hbar}{m} \langle \frac{\partial f}{\partial r_1} p_1^2 \rangle - \frac{i\hbar}{m} \langle \frac{\partial f}{\partial r_2} p_1 p_2 \rangle \\ &\quad - \frac{\hbar^2}{2m} \langle \left(\frac{\partial^2 f}{\partial r_1^2} + \frac{\partial^2 f}{\partial r_2^2} \right) p_1 \rangle - \frac{i\hbar}{m} \langle k_1^2 f r_1^{-3} \rangle \\ &\quad + i\hbar \left\langle f \left(\frac{\partial}{\partial r_1} (V_1 + V_{12}) \right) \right\rangle = 0. \end{aligned} \quad (17)$$

It is not possible to express this relation entirely in terms of the radial coordinates. For example, corresponding to eq. (9) we find that

$$\begin{aligned} \left\langle \frac{\partial^2 f}{\partial r_1^2} p_1 \right\rangle &= \frac{i\hbar}{2} \left\langle \frac{\partial^3 f}{\partial r_1^3} + \frac{\partial^3 f}{\partial r_1 \partial r_2^2} \right\rangle \\ &\quad - \left\langle \frac{\partial^2 f}{\partial r_1 \partial r_2} p_2 \right\rangle. \end{aligned} \quad (18)$$

However, if we let f be a function of r_i only, equation (17) simplifies to

$$\begin{aligned} \frac{1}{2m} \left\langle \frac{\partial f}{\partial r_i} p_i^2 \right\rangle + \frac{\hbar^2}{8m} \left\langle \frac{\partial^3 f}{\partial r_i^3} \right\rangle + \frac{1}{2m} \left\langle k_i^2 f r_i^{-3} \right\rangle \\ = \frac{1}{2} \left\langle f \left(\frac{\partial}{\partial r_i} (v_1 + v_{12}) \right) \right\rangle. \end{aligned} \quad (19)$$

We now specialize (19) by letting

$$f = r_i^n \quad (20)$$

where n is an integer. It is shown in the appendix that condition (2) is satisfied for an S state if

$$n \geq 1. \quad (21)$$

Equation (19) then becomes

$$\begin{aligned} \frac{n}{2m} \left\langle r_i^{n-1} p_i^2 \right\rangle + \frac{n(n-1)(n-2)\hbar^2}{8m} \left\langle r_i^{n-3} \right\rangle \\ + \frac{1}{2m} \left\langle k_i^2 r_i^{n-3} \right\rangle = \frac{1}{2} \left\langle r_i^n \left(\frac{\partial}{\partial r_i} (v_1 + v_2) \right) \right\rangle. \end{aligned} \quad (22)$$

We shall study eq. (22) in the next section.

The potential energy terms for the helium problem are given by

$$\begin{aligned} v_1 &= - \frac{2e^2}{r_1}, \\ v_2 &= - \frac{2e^2}{r_2}, \end{aligned} \quad (23)$$

and

$$v_{12} = \frac{e^2}{r_{12}}.$$

Then, when n is equal to one, equation (22) becomes

$$\begin{aligned} \langle T_1 \rangle &= \frac{1}{2} \langle r_1 \left(\frac{\partial}{\partial r_1} (V_1 + V_{12}) \right) \rangle \\ &= -\frac{1}{2} \langle V_1 + \frac{1}{2} V_{12} \rangle \end{aligned} \quad (24)$$

where T_1 is the kinetic energy of electron 1. Equation (24) is the one electron virial theorem.

S state helium functions may be completely expressed in terms of three variables, such as r_1 , r_2 , and θ_{12} (θ_{12} is the angle between \underline{r}_1 and \underline{r}_2). The S state helium Hamiltonian⁴ in terms of these coordinates is

$$\begin{aligned} H &= \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{\hbar^2}{2m} \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta} \frac{\partial}{\partial \theta_{12}} \left(\sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \right) \\ &+ V_1 + V_2 + V_{12} . \end{aligned} \quad (25)$$

The relations already derived in this section are valid for this Hamiltonian if we let

$$k_1^2 = k_2^2 = -\hbar^2 \frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \left(\sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \right) . \quad (26)$$

If we consider coordinate systems such as the Hylleraas r_1, r_2, r_{12} system⁵, we must be careful. The Hamiltonian may no longer have a simple dependence on the radial momenta. In r_1, r_2, r_{12} coordinates, the partial derivatives with respect to r_1 and r_2 are subject to the triangle equality, and the variations are no longer along the radial direction.

III. Scaling Helium Trial Functions

In sections I and II, we used the hypervirial theorem to derive expectation value relations for one and two electron central force hamiltonians. We now change our point of view, and consider

$$F(\Phi) = (\Phi, [H, W]\Phi) \quad (27)$$

as a functional of $\bar{\Phi}$. Then, because of the hypervirial theorem, if $\bar{\Phi}$ is equal to an exact bound state eigenfunction of H , $F(\bar{\Phi})$ will be identically equal to zero. If $\bar{\Phi}$ is equal to an approximate trial function with an adjustable parameter K , e.g.

$$\bar{\Phi} = \phi(K), \quad (28)$$

we may determine a value of K , say K_0 , such that

$$F(\phi(K_0)) = 0. \quad (29)$$

We then say that $\phi(K_0)$ satisfies the hypervirial theorem corresponding to W . In this section we choose K to be a scaling parameter, and adjust approximate ground state helium functions to satisfy the family of hypervirial theorems generated by

$$W_n = r_1^n p_1 \quad n = 1, 2, \dots \quad (30)$$

The helium atom hamiltonian in atomic units is

$$H = \frac{p_1^2}{2} + \frac{p_2^2}{2} + \frac{k_1^2}{2r_1^2} + \frac{k_2^2}{2r_2^2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \quad (31)$$

The $F_n(\bar{\Phi})$ corresponding to (30) are given by (22), and in atomic units are (within a multiplicative constant)

$$\begin{aligned} F_n(\bar{\Phi}) = & \frac{n}{2} (\bar{\Phi}, r_1^{n-1} p_1^2 \bar{\Phi}) + \frac{n(n-1)(n-2)}{8} (\bar{\Phi}, r_1^{n-3} \bar{\Phi}) \\ & + \frac{1}{2} (\bar{\Phi}, k_1^2 r_1^{n-3} \bar{\Phi}) \\ & - \frac{1}{2} (\bar{\Phi}, r_1^n \left(\frac{\partial}{\partial r_1} (V_1 + V_{12}) \right) \bar{\Phi}) \quad n = 1, 2, \dots \end{aligned} \quad (32)$$

We choose as our approximate trial function

$$\phi_{r,n} = N_{r,n} \left(e^{-K_{r,n}(\gamma r_1 + r_2)} + e^{-K_{r,n}(\gamma r_2 + r_1)} \right) \quad (33)$$

where $N_{\gamma, n}$ is the normalization constant;
 γ is a radial correlation parameter;
 $K_{\gamma, n}$ is the scale parameter, and is determined by the condition that

$$F_n(\phi_{\gamma, n}) = 0. \quad (34)$$

Eq. (34) may be explicitly solved for $K_{\gamma, n}$ giving

$$K_{\gamma, n} = \frac{\langle r_i^n \left(\frac{\partial}{\partial r_i} (V_1 + V_{12}) \right) \rangle_{\gamma}}{n \langle r_i^{n-1} p_i^2 \rangle_{\gamma} + \frac{n(n-1)(n-2)}{4} \langle r_i^{n-3} \rangle_{\gamma} + \langle k_i^2 r_i^{n-3} \rangle_{\gamma}} \quad (35)$$

where the subscript γ on the angular brackets means that the expectation values are evaluated using the unscaled function

$$\phi_{\gamma} = e^{-(\gamma r_1 + r_2)} + e^{-(\gamma r_2 + r_1)}.$$

We therefore generate a family of trial functions $\phi_{\gamma, n}$ corresponding to the family of hypervirial operators W_n .

When $n = 1$, our procedure corresponds to scaling a function to satisfy the virial theorem, and therefore $\phi_{\gamma, 1}$ will give the lowest energy for a given value of γ .⁶ When $\gamma = 1$, $\phi_{\gamma, 1}$ is equal to the Eckart-Kellner function^{7,8}; when $\gamma = 2.18/1.19$, $\phi_{\gamma, 1}$ is equal to the Eckart-Hylleraas radially correlated function^{5,7}.

In figure 1, we have plotted $K_{\gamma, n}$ versus n for $\gamma = 1$ and $\gamma = 2.18/1.19$. The values for n equals 1 thru 5 are given in table I. For both values of γ , $K_{\gamma, n}$ goes asymptotically to 1 as n becomes large. The curve for $\gamma = 2.18/1.19$, however, goes thru a maximum.

A series of curves for $\gamma \geq 1$ is shown in figure 2. For all values of $\gamma \geq 1$, $K_{\gamma, n}$ goes asymptotically to 1 as n becomes large. The behavior of $K_{\gamma, n}$ when $0 < \gamma \leq 1$ may be deduced by noting that

$$K_{\gamma, n} = \frac{1}{\gamma} K_{\frac{1}{\gamma}, n}. \quad (36)$$

We therefore conclude that

$$\lim_{n \rightarrow \infty} K_{\gamma, n} = \begin{cases} 1 & \text{when } \gamma \geq 1, \\ \frac{1}{\gamma} & \text{when } 0 < \gamma \leq 1. \end{cases} \quad (37)$$

Physically, this means that for large n and this choice of trial function, the hypervirial theorems generated by $W_n = r_1^n p_1$ are asymptotically satisfied when the most extended orbital becomes a hydrogen atom orbital. The convergence of (37) is more rapid the more localized the least extended orbital.

As stated above, $\phi_{\gamma, 1}$ gives the best value of the energy for a given value of γ . However, this does not imply that $\phi_{\gamma, 1}$ gives the best expectation values for other operators. As an example, we consider the positive powers of the radial coordinate of an electron in helium, r_1^t .

We have listed in table II values of $\langle r_1^t \rangle$ for $t = 1$ thru 5, which we have calculated using the Eckart-Hylleraas function^{5,7}, and the Eckart-Hylleraas function with $(2p)^2$ configuration interaction⁹. We have also given the accurate values for $\langle r_1 \rangle$ and $\langle r_1^2 \rangle$ calculated by Pekeris¹⁰. By comparing these numbers, it seems reasonable to assume that the true values of $\langle r_1^t \rangle$ are somewhat lower than the values calculated using the second function.

The values of $\langle r_1^t \rangle$ calculated using $\phi_{\gamma, n}$ for $\gamma = 1$ are given in table III. Numbers corresponding to t and n ranging from 1 thru 5 are given. The results for $\gamma = 2.18/1.19$ are given in table IV. The last column in both tables III and IV contains our estimates of the true values of $\langle r_1^t \rangle$ from table II. The first columns of expectation values in tables II and IV are identical because $\phi_{\gamma, n}$ is equal to the Eckart-Hylleraas function when $n = 1$ and $\gamma = 2.18/1.19$.

By comparing these numbers, we see that for both values of γ , the functions corresponding to $n = 2$ give the best overall values of $\langle r_1^t \rangle$. This is true, even though the functions corresponding to $n = 1$ give the best value of the energy. The results are particularly striking for $\gamma = 1$. The Eckart-Hylleraas function gives fairly reliable results for the first 5 positive powers of r_1 , however the

$n = 2$ function does give a noticeable improvement.

The expectation values of positive powers of the radial coordinate depend strongly on the behavior of the wave function in the region of configuration space where one electron is far from the nucleus. We conclude, therefore, that scaling approximate trial functions to satisfy the hypervirial theorem for $W = r_1^2 p_1$ improves their quality in this region of configuration space.

In contrast, scaling trial functions to satisfy the hypervirial theorem for $W = r_1 p_1$ improves their quality in the region of configuration space where both electrons are close to the nucleus. We may adjust $\Phi_{\gamma, n}$ to simultaneously satisfy the hypervirial theorems for $n = 1$ and 2 by treating γ as a variable. Then, γ is determined by the condition that

$$K_{\gamma, 1} = K_{\gamma, 2}. \quad (38)$$

We are, in effect, finding a value of γ which allows us to scale $\Phi_{\gamma, n}$ to simultaneously satisfy the hypervirial theorems generated by $W = r_1 p_1$ and $r_1^2 p_1$.

Equation (38) is satisfied when $\gamma = 1.822$ and $K = 1.195$. The resulting values of $\langle r_1^t \rangle$ are given in table V. For comparison, we list the values of $\langle r_1^t \rangle$ calculated using $\Phi_{\gamma, n}$ when $\gamma = 2.18/1.19$, and $n = 1$ and 2. We also list our estimates of the true values of $\langle r_1^t \rangle$ from table II. There is only a small difference between the values of $\langle r_1^t \rangle$ because $\gamma = 2.18/1.19 = 1.832$ almost satisfies (38). The calculated values of $\langle r_1^t \rangle$, however, are best when trial function (33) is scaled to simultaneously satisfy the first and second hypervirial theorems.

We may extend this procedure, and adjust trial functions to satisfy the first n hypervirial theorems by including n adjustable parameters. It is reasonable to expect further improvements in the expectation values of r_1^t . However, to verify this, we need reliable values for expectation values of higher powers of the radial coordinate in helium. We are presently learning how to obtain these numbers, and will report the results of these investigations at a later date.

Acknowledgment

The author acknowledges with thanks the many helpful discussions with Professor J. O. Hirschfelder during the course of this work.

Appendix

In this appendix we derive the limitations on η given by the inequalities (13) and (21). Acceptable hypervirial operators must satisfy equation (2). Let us define

$$D = (\psi, H W \psi) - (H \psi, W \psi). \quad (39)$$

Equation (2) then becomes

$$D = 0. \quad (40)$$

We use atomic units in the following discussion.

One Electron Central Force Problem

The hamiltonian is given by

$$H = -\frac{1}{2} \nabla^2 + V(r). \quad (41)$$

Substituting (41) into (39) we find that

$$D = -\frac{1}{2} (\psi, \nabla^2 W \psi) + \frac{1}{2} (\nabla^2 \psi, W \psi). \quad (42)$$

Singularities may occur at $r = 0$; therefore, we enclose the origin with a spherical surface S of infinitesimally small radius ϵ , and define D by its principal value. Therefore,

$$D = -\frac{1}{2} \lim_{\epsilon \rightarrow 0} \int_{\tau'} [\psi^* (\nabla^2 W \psi) - (W \psi) (\nabla^2 \psi)^*] d\tau \quad (43)$$

where τ' means that the integration is performed over all space except for the region enclosed by the spherical surface S . We may now apply Green's Theorem in the Second Form, then

$$D = \frac{1}{2} \lim_{\epsilon \rightarrow 0} \oint_S [\psi^* (\nabla W \psi) - (W \psi) (\nabla \psi^*)] \cdot d\mathbf{S} \quad (44)$$

The sign has changed because we consider the normal to the surface to be pointing away from the origin.

Equation (44) reduces to

$$D = \frac{1}{2} \lim_{\epsilon \rightarrow 0} \epsilon^2 \int_{r=\epsilon} [\psi^* (\frac{\partial}{\partial r} W \psi) - (W \psi) (\frac{\partial}{\partial r} \psi^*)] d\Omega \quad (45)$$

where the integration is over the solid angle. However

$$\psi = R(r) \Theta(\theta, \phi), \quad (46)$$

and therefore

$$D = \frac{1}{2} \lim_{\epsilon \rightarrow 0} \epsilon^2 [R (\frac{d}{dr} W R) - (W R) (\frac{d}{dr} R)]_{r=\epsilon} \quad (47)$$

We let

$$W = r^n p = \frac{1}{i} r^{n-1} \frac{d}{dr} (r \quad) . \quad (48)$$

Substituting (48) into (47) and expanding we obtain

$$D = \frac{1}{2i} \lim_{\epsilon \rightarrow 0} [(n-1) R^2 \epsilon^n + n R \frac{dR}{dr} \epsilon^{n+1} + (R \frac{d^2 R}{dr^2} - (\frac{dR}{dr})^2) \epsilon^{n+2}]_{r=\epsilon} . \quad (49)$$

We assume that

$$\lim_{r \rightarrow 0} r^2 V(r) = 0 . \quad (50)$$

Then, near the origin¹¹

$$R = A r^l + o(r^{l+1}), \quad (51)$$

where A is a constant, and $o(r^l)$ stands for an expression which satisfies the condition that

$$\lim_{r \rightarrow 0} \frac{o(r^s)}{r^s} = c, \quad (52)$$

where c is a constant (which may be zero). Substituting (51) into (49) we find that

$$D = \frac{1}{2i} \lim_{\epsilon \rightarrow 0} [A^2 (\ell+1)(n-1) \epsilon^{n+2\ell} + o(\epsilon^{n+2\ell+1})] \quad (53)$$

Therefore, $D = 0$ when $n+2\ell \geq 1$, or $n \geq 1-2\ell$. This proves inequality (13).

Two Electron Central Force Problem (S state)

The hamiltonian is given by

$$H = -\frac{1}{2} \nabla_1^2 - \frac{1}{2} \nabla_2^2 + V_1(r_1) + V_2(r_2) + V_{12}(r_{12}) \quad (54)$$

For an S state, Ψ is real. Therefore, analogously to (44)

$$D = \frac{1}{2} \lim_{\epsilon \rightarrow 0} \int_{T_2} [\oint_{S_1} \{ \Psi(\nabla_1 W \Psi) - (W \Psi)(\nabla_1 \Psi) \} \cdot d\underline{S}_1] \quad (55)$$

$$+ \frac{1}{2} \lim_{\epsilon \rightarrow 0} \int_{T_1} [\oint_{S_2} \{ \Psi(\nabla_2 W \Psi) - (W \Psi)(\nabla_2 \Psi) \} \cdot d\underline{S}_2] .$$

We let

$$W = \frac{1}{i} r_1^n p_1 = \frac{1}{i} r_1^{n-1} \frac{\partial}{\partial r_1} (r_1) \quad (56)$$

Then, corresponding to (49)

$$D = D_1 + D_2, \quad (57)$$

where

$$D_1 = \frac{1}{2i} \lim_{\epsilon \rightarrow 0} \int_{r_2} d\tau_2 \left[\left\{ (n-1) \epsilon^n \psi^2 + n \epsilon^{n+1} \psi \frac{\partial \psi}{\partial r_1} + \epsilon^{n+2} \left(\psi \frac{\partial^2 \psi}{\partial r_1^2} - \left(\frac{\partial \psi}{\partial r_1} \right)^2 \right) \right\}_{r_1 = \epsilon} d\Omega_1 \right]$$

and

$$D_2 = \frac{1}{2i} \lim_{\epsilon \rightarrow 0} \int_{r_1} d\tau_1 \left[\left\{ \epsilon^{n+2} \left(\psi \frac{\partial^2 \psi}{\partial r_1 \partial r_2} - \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_2} \right) \right\}_{r_2 = \epsilon} d\Omega_2 \right].$$

For an S state, if

$$\lim_{r_1 \rightarrow 0} r_1^2 V_1(r_1) = 0, \quad (58)$$

$$\lim_{r_2 \rightarrow 0} r_2^2 V_2(r_2) = 0,$$

and

$$\lim_{r_{12} \rightarrow 0} r_{12} V_{12}(r_{12}) = \text{constant which may be zero,}$$

then ψ is a non zero finite function of r_2 when r_1 is zero, and vice versa.^{10,12} If we also assume this to be true of the partial derivatives of ψ , then

$$D_1 = \frac{1}{2i} \lim_{\epsilon \rightarrow 0} \left\{ A(n-1)\epsilon^n + o(\epsilon^{n+1}) \right\}$$

and

$$D_2 = \frac{1}{2i} \lim_{\epsilon \rightarrow 0} \left\{ A' \epsilon^{n+2} + o(\epsilon^{n+3}) \right\}.$$

Here, A and A' are non zero constants.

Therefore, $D = 0$ for an S state if $n \geq 1$, which proves inequality (21).

References

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Table I.

$K_{\nu,n}$ as calculated from equation (35).

n	$K_{1,n}$	$K_{2.18/1.19,n}$
1	1.688	1.191
2	1.500	1.193
3	1.344	1.266
4	1.227	1.444
5	1.145	1.744

Table II.

$\langle r_1^t \rangle$ as calculated from three helium ground state wave functions.

	$\langle r_1^t \rangle$ in atomic units		
t	Eckart-Hylleraas ^{5,7}	Eckart-Hylleraas with $(2p)^2$ C.I. ⁹	Pekeris ¹⁰
1	0.94	0.93	0.9295
2	1.24	1.22	1.1935
3	2.14	2.10	
4	4.66	4.53	
5	12.28	11.81	

Table III.

$\langle r_1^t \rangle$ as calculated from $\Phi_{\gamma, n}$ with $\gamma = 1$. Each column gives values of $\langle r_1^t \rangle$ corresponding to a definite value of n . The value of n is given at the top of the column. The last column gives our estimates of the true values of $\langle r_1^t \rangle$ from table II.

$\langle r_1^t \rangle$ in atomic units						
n						
t	1	2	3	4	5	estimated
1	0.89	1.00	1.12	1.22	1.31	0.93
2	1.05	1.33	1.66	1.99	2.29	1.19
3	1.56	2.22	3.09	4.06	5.00	< 2.1
4	2.77	4.44	6.90	9.94	13.11	< 4.5
5	5.76	10.37	17.97	28.37	40.10	< 11.8

Table IV.

$\langle r_1^t \rangle$ as calculated from $\Phi_{\gamma, n}$ with $\gamma = 2.18/1.19 = 1.832$. The arrangement of this table is the same as table III.

$\langle r_1^t \rangle$ in atomic units						
n						
t	1	2	3	4	5	estimated
1	0.938	0.936	0.88	0.77	0.64	0.930
2	1.24	1.23	1.09	0.84	0.58	1.19
3	2.14	2.13	1.78	1.20	0.68	< 2.1
4	4.66	4.63	3.64	2.16	1.01	< 4.5
5	12.28	12.17	9.03	4.68	1.82	< 11.8

Table V.

$\langle r_1^t \rangle$ as calculated from $\phi_{\gamma, n}$ with $\gamma = 2.18/1.19$ and 1.822. The last column gives our estimates of the true values of $\langle r_1^t \rangle$ from table II.

	$\langle r_1^t \rangle$ in atomic units			
	$\gamma = 2.18/1.19 = 1.832$		$\gamma = 1.822$	
t	n = 1	n = 2	n = 1 and 2	estimated
1	0.938	0.936	0.936	0.930
2	1.236	1.231	1.231	1.19
3	2.143	2.130	2.128	< 2.1
4	4.66	4.63	4.61	< 4.5
5	12.28	12.17	12.11	< 11.8

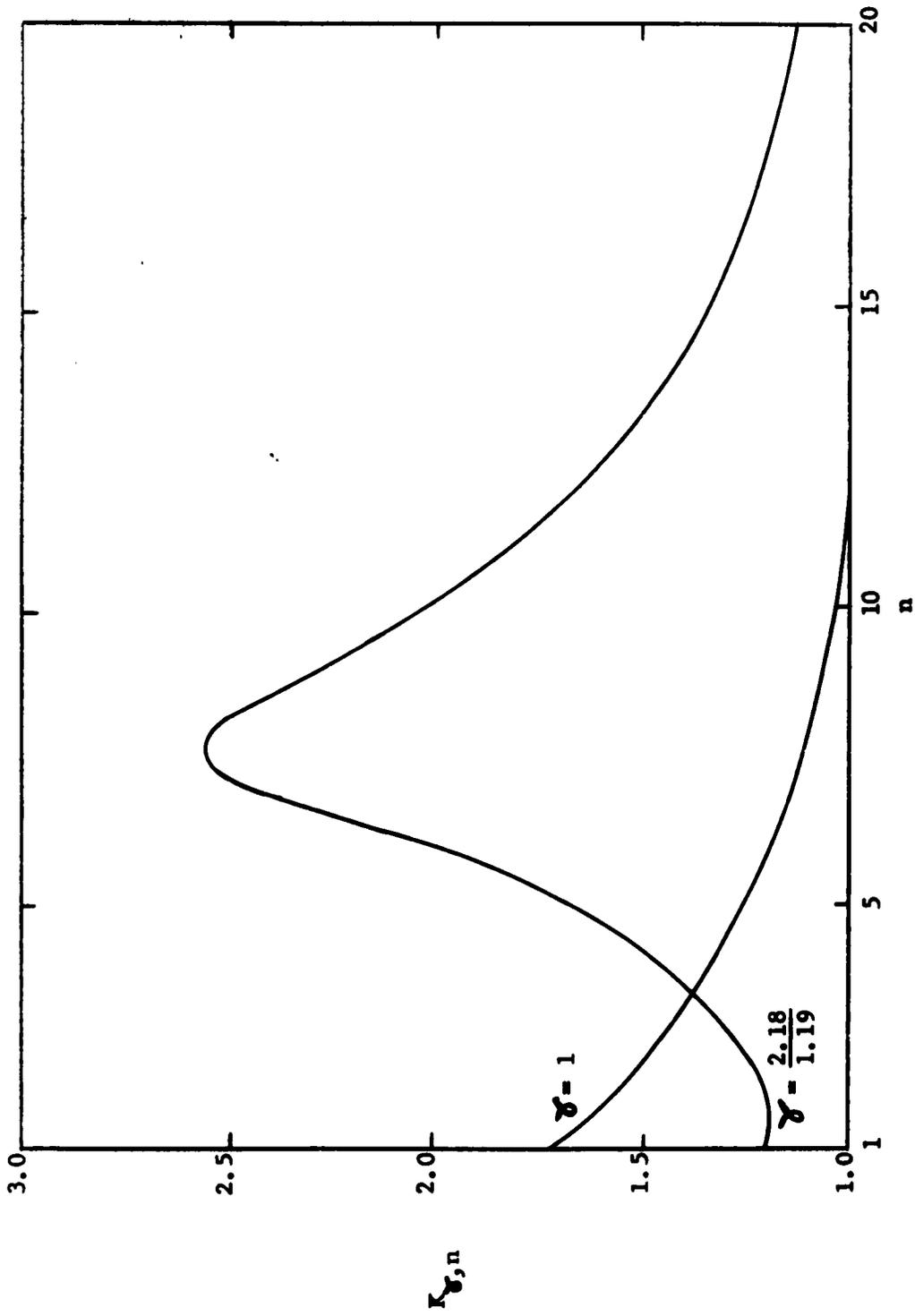


Figure 1. $K_{\gamma,n}$ versus n for $\gamma = 1$ and $\gamma = 2.18/1.19$.

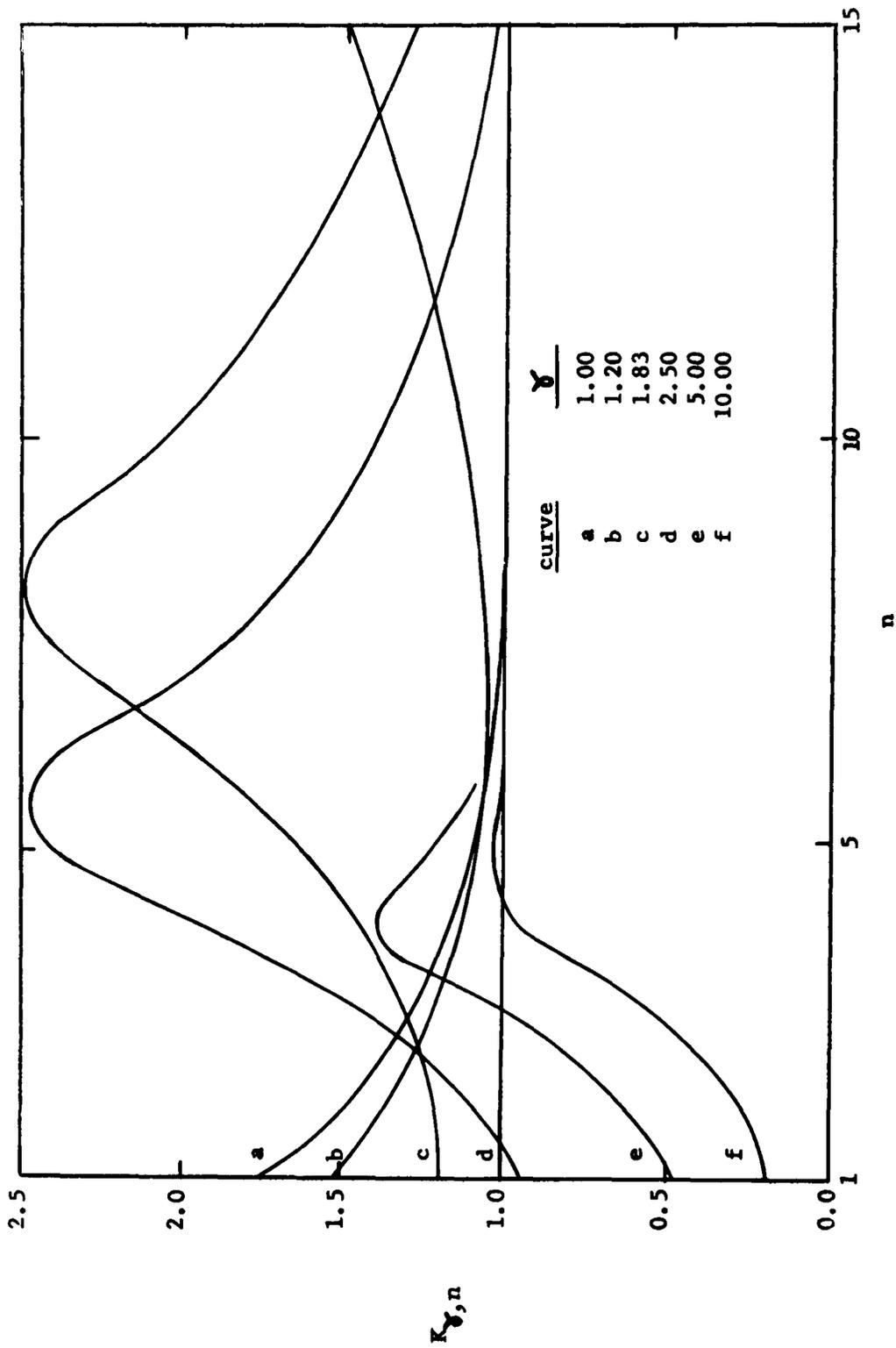


Figure 2. $K_{g,n}$ versus n for several values of γ . The values of γ corresponding to the curves are given in the table.