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ABSTRACT

Expectation values of properties other than energy are calculated for the ground state of the two-electron atom with arbitrary nuclear charge. The calculations are designed to test the use of simple wave functions with embedded screening constants, where different screening constants are used for different properties. The results are compared with the perturbation expansion of Scherr and Knight, who have determined a large number of properties correct through sixth order.

Dalgarno has suggested that a screening constant be chosen so as to make the first order perturbation correction vanish for the property under consideration. Robinson has shown that this choice is equivalent to the requirement that the zeroth order wave function satisfy a hypervirial relation, where the hypervirial generator is related to the property through a differential equation. This procedure gives excellent numerical results for properties having positive definite operators.

For one-electron properties with positive definite operators, Dalgarno's method gives expectation values which are too small. When

applicable, slight improvements are obtained by maximizing the expectation value calculated with the zeroth plus first order wave functions.

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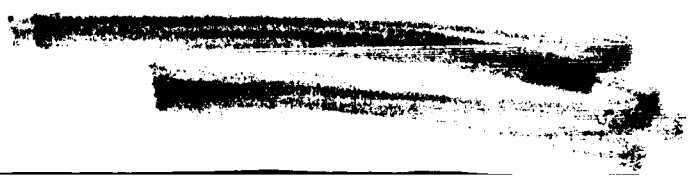

I. INTRODUCTION

One of the most important problems in quantum mechanics is the calculation of accurate expectation values of properties other than energy. It remains an open question whether it is necessary to use Hartree-Fock wave functions for such calculations. We have explored the possibility of using simpler wave functions with embedded screening constants, where different screening constants are used for the calculation of different properties. The properties of the family of two-electron atoms (and ions) provide a convenient test of the numerical accuracy of different methods of calculation. As a basis of comparison we use the calculations of Scherr and Knight,[1] which are based on a perturbation expansion in powers of one over the nuclear charge. They have determined a large number of properties accurate through the sixth order.

Dalgarno[2] has suggested that a screening constant be chosen so as to make the first order perturbation correction vanish for the property under consideration. Robinson[3] has shown that this choice is equivalent to the requirement that the zeroth order wave function satisfy a hypervirial relation, where the hypervirial generator is related to the property through a differential equation. The Dalgarno procedure gives excellent numerical results when applied to the calculation of properties represented by positive definite operators.

If the wave function contains two or more embedded screening constants, additional constraints are necessary if the choice of screening constants is to be unique. Many such constraints suggest themselves, such as minimizing the energy, satisfying the virial

theorem, etc., but at the present time we can suggest no systematic method for choosing the best set of constraints.

For those one-electron properties associated with positive definite operators, the Dalgarno procedure gave expectation values which were too small. This suggested maximizing the expectation value calculated with the zeroth plus first order wave functions. In some cases slight improvements were obtained in this way, but the amount of additional work required casts some doubt on the practicality of the method.

The idea of using different screening constants for different properties dates back to the early days of quantum mechanics. In 1927 Pauling[4] proposed a systematic procedure for determining the screening constants. His method was applicable to any property which, for a hydrogen-like atom, would vary as some power of Z and as some other power of the principal quantum number. He predicted rather accurately the mole refraction, diamagnetic susceptibility, atomic scattering factors,[5] etc., for atoms and ions throughout the whole periodic table. Unfortunately, Pauling's method of adjusting the screening constants does not seem to be currently applicable. However, the principle still remains valid that the screening is small near the nucleus and becomes large at large separations. Thus, as is shown in Fig. 1, the optimum screening constant for calculating the expectation value of $1/r^2$ is much smaller than the screening constant required for the expectation value of r^2.

II. THE PERTURBATION EXPANSION

The Hamiltonian operator for the two-electron atom with nuclear charge Z is

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - Z\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} \quad , \tag{1}$$

where the unit of length is the Bohr radius, a_o , and the energy is measured in units of e^2/a_o (e is the electronic charge). Introducing a "screening parameter", S , the Hamiltonian may be written in the equivalent form

$$H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - (Z-S)\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{1}{r_{12}} - S\left(\frac{1}{r_1} + \frac{1}{r_2}\right). \tag{2}$$

If we make the change of variable $\rho = (Z-S)r$ and measure the energy in units of $(Z-S)^2 e^2/a_o$, Eq. (2) may be expressed in the reduced form

$$H = H_o + \frac{1}{Z-S} V_1 + \frac{S}{Z-S} V_2 \quad , \tag{3}$$

where

$$H_o = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{1}{\rho_1} - \frac{1}{\rho_2} \quad , \tag{4}$$

$$V_1 = \frac{1}{\rho_{12}} \quad , \tag{5}$$

and

$$V_2 = -\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) . \tag{6}$$

Eq. (3) defines a double perturbation problem[6] with the natural parameters $1/(Z-S)$ and $S/(Z-S)$. The total wave function is expanded in the double power series

$$\Psi = \sum_{j=0}^{\infty} \sum_{k=0}^{\infty} \frac{1}{(Z-S)^j} \frac{S^k}{(Z-S)^k} \varphi^{(j,k)} , \tag{7}$$

where the unperturbed function is simply

$$\varphi^{(0,0)} = \frac{1}{\pi} e^{-(\rho_1+\rho_2)} . \tag{8}$$

The $\varphi^{(j,k)}$ do not depend upon the value of the parameter S .

We wish to calculate the expectation value $\langle W \rangle$ of an operator W which is a homogeneous function of the coordinates of degree α . Since the screening constant S does not occur either in the unreduced Hamiltonian, Eq. (1), or in W itself, the value of $\langle W \rangle$ cannot depend upon the value of S . In the reduced units, W is designated by w , so that

$$W = (Z-S)^{\alpha} w . \tag{9}$$

The expectation value of w is expressed by the symbol $\langle w;S \rangle$, which stresses its dependence upon the value of S . The expectation value $\langle W \rangle$ is then given by the double power series

$$\langle W \rangle = (Z-S)^{\alpha} \langle w; S \rangle$$

$$= (Z-S)^{\alpha} \sum_{j=0}^{\infty} \sum_{K=0}^{\infty} \frac{1}{(Z-S)^j} \frac{S^K}{(Z-S)^K} \langle w \rangle_{j,K}$$

$$= (Z-S)^{\alpha} \sum_{n=0}^{\infty} \frac{1}{(Z-S)^n} \sum_{K=0}^{n} S^K \langle w \rangle_{n-K,K} \quad , \tag{10}$$

where

$$\langle w \rangle_{j,K} = \sum_{\mu=0}^{j} \sum_{\nu=0}^{K} \langle \varphi^{(\mu,\nu)} | w | \varphi^{(j-\mu,K-\nu)} \rangle \, . \tag{11}$$

The $\langle w \rangle_{j,K}$ are independent of S (since S does not occur in either $\varphi^{(j,K)}$ or w).

Alternately, we can rewrite Eq. (10) in the form

$$\langle W \rangle = (Z-S)^{\alpha} \sum_{n=0}^{\infty} \frac{1}{(Z-S)^n} \langle w; S \rangle_n \quad , \tag{12}$$

where

$$\langle w; S \rangle_n = \sum_{K=0}^{n} S^K \langle w \rangle_{n-K,K} \quad . \tag{13}$$

In Sec. III, the $\langle w; S \rangle_n$ are obtained directly as the n-th order terms in $\langle w; S \rangle$, where S is regarded as a constant and the perturbation is $V_1 + S V_2$.

In order to compare the results of the $V_1 + S V_2$ perturbation calculations with the $1/Z$ expansions of Scherr and Knight,[1b]

it is convenient to expand Eq. (10) in a double power series in S and $1/Z$. Thus

$$\langle W \rangle = Z^{\alpha} \sum_{K=0}^{\infty} \frac{1}{Z^K} \sum_{m=0}^{K} S^m A_{K,m}(\alpha) \quad , \tag{14}$$

where

$$A_{K,m}(\alpha) = \sum_{\ell=0}^{m} \frac{(-1)^{\ell}(\alpha+\ell-K)!}{(\alpha-K)!\,\ell!} \langle w \rangle_{K-m,m-\ell} \quad , \quad K \lesssim \alpha \, , \tag{15a}$$

and

$$A_{K,m}(\alpha) = \sum_{\ell=0}^{m}{}' \frac{(K-\alpha-1)!}{(K-\ell-\alpha-1)!\,\ell!} \langle w \rangle_{K-m,m-\ell} \quad , \quad K > \alpha \, . \tag{15b}$$

The prime indicates that the summation is taken only over terms involving non-negative factorials.

Since $\langle W \rangle$ is independent of S , we see immediately from (14) that

$$\langle W \rangle = Z^{\alpha} \sum_{K=0}^{\infty} \frac{1}{Z^K} A_{K,0}(\alpha) = Z^{\alpha} \sum_{K=0}^{\infty} \frac{1}{Z^K} \langle w \rangle_{K,0} \quad , \tag{16}$$

which is in agreement with the result obtained by setting $S = 0$ in Eq. (10). Furthermore,

$$\sum_{m=1}^{K} S^m A_{K,m}(\alpha) = 0 \quad , \quad K = 1, 2, 3, \cdots \tag{17}$$

independently of the value of S , so that

$$A_{K,m}(\alpha) = 0 \quad ; \quad K = 1, 2, 3, \cdots \; ; \; m = 1, 2, \cdots, K. \tag{18}$$

These conditions make it possible to express all the $\langle w \rangle_{n-K,K}$ in terms of the $\langle w \rangle_{n-K,0}$. For example, for the case $\alpha < 0$ we have, from Eq. (15b),

$$A_{K+j,j} = \sum_{\ell=0}^{j}{}' \frac{(K+j-\alpha-1)!}{(K+j-\alpha-\ell-1)!\,\ell!} \langle w \rangle_{K,j-\ell} = 0 \quad , \; j = 1, 2, 3, \cdots, \tag{19}$$

so that

$$\langle w \rangle_{K,j} = -\sum_{m=0}^{j-1}{}' \frac{(K+j-\alpha-1)!}{(K+m-\alpha-1)!\,(j-m)!} \langle w \rangle_{K,m} \quad . \tag{20}$$

Repeated application of Eq. (20) then leads to the relation

$$\langle w \rangle_{n-K,K} = \frac{(-1)^K (n-\alpha-1)!}{(n-\alpha-K-1)!\,K!} \langle w \rangle_{n-K,0} \quad , \tag{21}$$

and therefore Eq. (10) may be rewritten in the form

$$\langle W \rangle = (z-S)^{\alpha} \sum_{n=0}^{\infty} \frac{1}{(z-S)^n} \sum_{K=0}^{n} \frac{(-1)^K (n-\alpha-1)!}{(n-\alpha-1-K)!\,K!} S^K \langle w \rangle_{n-K,0} \quad , \alpha < 0. \tag{22}$$

The case $\alpha \geq 0$ is somewhat more complicated. However, by using Eq. (15a) or Eq. (15b), as appropriate, it is possible to show that

$$\langle W \rangle = (z-S)^{\alpha} \Bigg[\sum_{n=0}^{\alpha} \frac{1}{(z-S)^n} \sum_{K=0}^{n} \frac{(\alpha-n+K)!}{(\alpha-n)!\,K!} S^K \langle w \rangle_{n-K,0} +$$

$$+ \sum_{n=\alpha+1}^{\infty} \frac{1}{(z-S)^n} \sum_{K=0}^{n-\alpha-1} \frac{(-1)^K (n-\alpha-1)!}{(n-\alpha-1-K)!\,K!} S^K \langle w \rangle_{n-K,0} \Bigg] \quad , \alpha \geq 0. \tag{23}$$

Therefore, in order to obtain the expansion of the expectation value $\langle W \rangle$ in either of the alternate forms (12) or (16), it is only necessary to evaluate the matrix elements

$$\langle w \rangle_{j,0} = \sum_{\mu=0}^{j} \langle \varphi^{(\mu,0)} | w | \varphi^{(j-\mu,0)} \rangle . \qquad (24)$$

Scherr and Knight[1] have computed the functions $\varphi^{(\mu,0)}$ through $\mu = 6$ by a variational method and have tabulated the matrix elements $\langle w \rangle_{j,0}$ for a number of operators through $j = 6$.* In several cases they were able to check their results with coefficients obtained by analysis of the best available variational wave function and the agreement was found to be very good.

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* The values of these matrix elements for most of the properties they considered are included in Table V.

III. DALGARNO'S METHOD

In order to determine directly the coefficients $\langle w;S\rangle_n$ in Eq. (12), it is convenient to rewrite the Hamiltonian (3) in the form

$$H = H_0 + \frac{1}{(Z-S)}\left(V_1 + S V_2\right), \tag{25}$$

where S is assumed constant and $1/(Z-S)$ is the perturbation parameter. If the total wave function is expanded in the power series

$$\Psi = \sum_{K=0}^{\infty} \frac{1}{(Z-S)^K}\,\varphi^{(K)}, \tag{26}$$

the expectation value $\langle w;S\rangle$ may then be written in the form

$$\langle w;S\rangle = \sum_{n=0}^{\infty} \frac{1}{(Z-S)^n} \sum_{K=0}^{n} \langle \varphi^{(K)} | w | \varphi^{(n-K)}\rangle, \tag{27}$$

so that

$$\langle w;S\rangle_n = \sum_{K=0}^{n} \langle \varphi^{(K)} | w | \varphi^{(n-K)}\rangle. \tag{28}$$

The $\varphi^{(K)}$, which are related to the functions $\varphi^{(j,K)}$ by the expression

$$\varphi^{(K)} = \sum_{j=0}^{K} S^j \varphi^{(K-j,j)}, \tag{29}$$

may be obtained, in principle, by the methods of standard perturbation theory.[6]

If the series in Eq. (12) is truncated after a finite number of terms, the resulting expectation value is a function of the screening parameter S. As discussed in the introduction, there is a best value of S for each operator W (usually not the energy-optimized screening constant). Unfortunately, there is no general variation principle for the expectation values of operators other than the Hamiltonian, so that we do not have a firm basis for choosing S.

In the ordinary variational calculation of the energy, the expectation value of the Hamiltonian (25) is made stationary with respect to first order variations of the wave function.[7] This is equivalent to choosing the screening constant so that the first order perturbation energy

$$\epsilon_1 = \langle \varphi^{(0)} | V_1 + S V_2 | \varphi^{(0)} \rangle \tag{30}$$

is zero. For cases in which the first order correction to the expectation value of the observable W can be obtained explicitly, Dalgarno and Stewart[2] have suggested that the appropriate value of the screening parameter to be used in calculating $\langle W \rangle$ is simply the one which makes the first order correction $\langle w; S \rangle_1$ vanish.

From Eq. (28), the first order coefficient $\langle w; S \rangle_1$ is

$$\langle w; S \rangle_1 = \langle \varphi^{(0)} | w | \varphi^{(1)} \rangle + \langle \varphi^{(1)} | w | \varphi^{(0)} \rangle, \tag{31}$$

where $\varphi^{(1)}$ is a solution of the differential equation

$$(H_0 - \epsilon_0)\varphi^{(1)} + (V_1 + sV_2 - \epsilon_1)\varphi^{(0)} = 0 \tag{32}$$

with the orthogonality condition

$$\langle \varphi^{(1)} | \varphi^{(0)} \rangle + \langle \varphi^{(0)} | \varphi^{(1)} \rangle = 0 \ . \tag{33}$$

Because of the form of V_1 , Eq. (32) cannot be solved explicitly. However, according to the Dalgarno Interchange Theorem,[8] Eq. (31) may be replaced by

$$\langle w; s \rangle_1 = \langle \varphi^{(0)} | V_1 + sV_2 | \psi^{(1)} \rangle + \langle \psi^{(1)} | V_1 + sV_2 | \varphi^{(0)} \rangle \ , \tag{34}$$

where $\psi^{(1)}$ is a solution of the equation

$$(H_0 - \epsilon_0)\psi^{(1)} + (w - \langle w \rangle_{0,0})\varphi^{(0)} = 0 \tag{35}$$

with an orthogonality condition similar to (33).

If w is a one-electron operator, Eq. (35) can often be solved analytically. Following Dalgarno, it is assumed that $\psi^{(1)}$ may be written in the form

$$\psi^{(1)} = F\varphi^{(0)} \ , \tag{36}$$

where F is some function of the coordinates. From Eq. (35) it follows that F must satisfy the differential equation

$$(H_0 - \epsilon_0) F \varphi^{(0)} + (w - \langle w \rangle_{0,0}) \varphi^{(0)} = 0 \ . \tag{37}$$

If w is a function only of the radial coordinate ρ_1 , Eq. (37) is separable and F may be obtained by direct integration of the equation

$$\frac{\partial}{\partial \rho_1} \left(\rho_1^2 \varphi^{(0)2} \frac{dF}{d\rho_1} \right) = 2 \rho_1^2 (w - \langle w \rangle_{0,0}) \varphi^{(0)2} \ . \tag{38}$$

Gordon[9] has carried out the explicit derivation of $\langle w; S \rangle_1$ for the case in which w is a positive integral power of the radial coordinate. He was able to solve Eq. (38) readily for $w = \rho_1^n$, obtaining the expression

$$F(\rho_1) = \frac{\langle \rho_1^n \rangle_{0,0}}{2} \sum_{K=1}^{n} \left[\frac{K+3}{K+1} - \frac{2^{K+2} \rho_1^K}{(K+1)(K+2)!} \right] , \quad n > 0 , \tag{39}$$

where $\langle \rho_1^n \rangle_{0,0} = (n+2)!/2^{n+1}$. He could then calculate the expectation value $\langle r_1^n \rangle$ explicitly through first order. In the ordinary units defined in the first paragraph of Sec. II, the result is

$$\langle r_1^n \rangle_D = \frac{\langle \rho_1^n \rangle_{0,0}}{(Z-S)^n} \left[1 + \frac{n(S_n - S)}{Z - S} \right] , \quad n > 0 , \tag{40}$$

where the subscript D is used to designate an expectation value which is correct through first order and where

$$S_n = \frac{5}{8} - \frac{1}{4n}\left[\sum_{K=1}^{n}\frac{3}{K+1} - \sum_{K=1}^{n}\frac{K+7}{2^{K+2}(K+1)}\right] . \qquad (41)$$

The first order term in Eq. (40) vanishes if S is set equal to S_n. The value of S_n increases monotonically from $3/8$ for $n=1$ toward a limit of $5/8$ as n becomes infinite. These results are to be compared with the energy-optimized value[7] $S_E = 5/16$.

The same procedure may also be applied to other one-electron operators. For example, for $w = 1/\rho_1$, integration of Eq. (38) yields

$$F(\rho_1) = \rho_1 - \frac{3}{2} , \qquad (42)$$

so that

$$\left\langle \frac{1}{r_1} \right\rangle_D = (Z-S)\left\langle \frac{1}{\rho_1} \right\rangle_D = (Z-S)\left[1 + \frac{1}{(Z-S)}\left(S - \frac{5}{16}\right)\right] = Z - \frac{5}{16} . \qquad (43)$$

The value of the screening constant which satisfies the Dalgarno criterion is $S_{-1} = 5/16$, in agreement with the energy-optimized value. Note, however, that the expectation value of $1/r_1$ is independent of S through first order.

Similarly, for $w = 1/\rho_1^2$,

$$F(\rho_1) = 2\left(\rho_1 + \ln\rho_1 + \gamma + \ln 2 - 3\right) , \qquad (44)$$

where $\gamma = 0.577216$ is Euler's constant, and

$$\left\langle \frac{1}{r_1^2} \right\rangle_D = (z-S)^2 \left\langle \frac{1}{\rho_1^2} \right\rangle_D = 2(z-S)^2 \left[1 + \frac{1}{(z-S)} \left(\frac{3}{4} \ln 2 - \frac{17}{16} + 2S \right) \right]. \quad (45)$$

The value of S which makes the first order term vanish is

$$S_{-2} = \frac{17}{32} - \frac{3}{8} \ln 2 = 0.27132. \quad (46)$$

Finally, for $w = \delta(\vec{\rho}_1)$,

$$\pi F(\rho_1) = \ln \rho_1 + \rho_1 - \frac{1}{2\rho_1} + \gamma + \ln 2 - 5/2 \quad (47)$$

and[2]

$$\pi \langle \delta(\vec{r}_1) \rangle_D = (z-S)^3 \pi \langle \delta(\vec{\rho}_1) \rangle_D = (z-S)^3 \left[1 + \frac{3}{(z-S)} \left(\frac{1}{4} \ln 2 - \frac{19}{48} + S \right) \right]. \quad (48)$$

The value of S determined by Dalgarno's method is

$$S_\delta = \frac{19}{48} - \frac{1}{4} \ln 2 = 0.22255. \quad (49)$$

In Sec. II it was shown that the coefficients $\langle w; S \rangle_n$ of the $1/(z-S)$ expansion of the expectation value $\langle W \rangle$ may be written in terms of the coefficients $\langle w \rangle_{K,o}$ of the $1/z$ expansion. Through first order, Eqs. (22) and (23) both give

$$\langle W \rangle_D = (z-S)^\alpha \left[\langle w \rangle_{0,0} + \frac{1}{(z-S)} \left(\langle w \rangle_{1,0} + \alpha S \langle w \rangle_{0,0} \right) \right]. \quad (50)$$

Dalgarno's choice of the screening parameter is, therefore,

$$S_w = -\frac{\langle w\rangle_{1,0}}{\alpha\langle w\rangle_{0,0}} \tag{51}$$

and the expectation value correct through first order in this approximation is simply

$$\langle W\rangle_D = \langle w\rangle_{0,0}\left[Z + \frac{\langle w\rangle_{1,0}}{\alpha\langle w\rangle_{0,0}}\right]^{\alpha} . \tag{52}$$

The relation (52) makes it possible to evaluate the accuracy of the first order screening approximation for all the operators treated by Scherr and Knight without having to solve Eq. (35). Expanding Eq. (52) in powers of $1/Z$, we obtain

$$\langle W\rangle_D = Z^{\alpha}\langle w\rangle_{0,0}\sum_{K=0}^{\infty}\frac{(-\alpha+K-1)!}{(-\alpha)^K(-\alpha-1)!\,K!}\left(\frac{\langle w\rangle_{1,0}}{\langle w\rangle_{0,0}}\right)^K\frac{1}{Z^K} \quad , \quad \alpha < 0 \tag{53}$$

and

$$\langle W\rangle_D = Z^{\alpha}\langle w\rangle_{0,0}\sum_{K=0}^{\alpha}\frac{\alpha!}{\alpha^K(\alpha-K)!\,K!}\left(\frac{\langle w\rangle_{1,0}}{\langle w\rangle_{0,0}}\right)^K\frac{1}{Z^K} \quad , \quad \alpha > 0 . \tag{54}$$

The coefficients of $1/Z^K$ in Eqs. (53) and (54) may then be compared with the $\langle w\rangle_{K,0}$ tabulated by Scherr and Knight. In all cases the first two coefficients are given exactly.

It is easy to verify that the Dalgarno criterion makes the first order expectation value stationary. Differentiating partially with respect to S,

$$\frac{\partial}{\partial S}\langle W\rangle_D = -(\alpha-1)(Z-S)^{\alpha-2}\left(\langle w\rangle_{1,0} + \alpha S\langle w\rangle_{0,0}\right). \tag{55}$$

The first derivative is zero if S is given by Eq. (51) and vanishes identically for $\alpha = 1$. Furthermore, differentiating once again and setting $S = S_w$,

$$\left[\frac{\partial^2}{\partial S^2}\langle W\rangle_D\right]_{S=S_w} = -\alpha(\alpha-1)(Z-S_w)^{\alpha-2}\langle w\rangle_{0,0} . \tag{56}$$

This expression is negative if $\langle w\rangle_{0,0}$ is positive and vice versa. Therefore, Dalgarno's method maximizes the first order expectation value of any positive operator which is a homogeneous function of the coordinates.

Expectation values calculated by the methods discussed in this section are tabulated in Sec. VI. There is one interesting result, however, which should be mentioned at this point. For the case in which W is a positive power of the radial coordinate, with $\alpha = -n$, all the coefficients tabulated by Scherr and Knight satisfy the inequality

$$\frac{(n+K-1)!}{n^K(n-1)!\,K!}\,\frac{\langle \rho_1^n\rangle_{1,0}^K}{\langle \rho_1^n\rangle_{0,0}^{K-1}} \leq \langle \rho_1^n\rangle_{K,0} \tag{57}$$

(see Table V). Therefore, Dalgarno's criterion apparently yields a valid lower bound for the expectation value $\langle r_1^n\rangle$ for positive integral n . This observation forms the basis of the alternate method discussed in Sec. V.

IV. EQUIVALENCE OF DALGARNO AND HYPERVIRIAL METHODS

As Robinson has shown,[3] the Dalgarno method of requiring that $\langle w; S\rangle_1 = 0$ is equivalent to satisfying a certain hypervirial theorem[10]

$$\langle \varphi^{(0)} | [H, L] | \varphi^{(0)} \rangle = 0 \ . \tag{58}$$

Here L is an anti-Hermitian operator associated with the property W.

For a system perturbed by a potential V, we have, from Eq. (34),

$$\langle w; S\rangle_1 = \langle \varphi^{(0)} | V | \psi^{(1)} \rangle + \langle \psi^{(1)} | V | \varphi^{(0)} \rangle , \tag{59}$$

where $\psi^{(1)}$ is defined by Eq. (35). In the Dalgarno method, $\psi^{(1)} = F\varphi^{(0)}$, where F is a function. However, we might equally well take $\psi^{(1)} = L\varphi^{(0)}$, where L is an anti-Hermitian operator, $L^\dagger = -L$. Then, since $\langle \varphi^{(0)} | [H_0, L] | \varphi^{(0)} \rangle = 0$, Eq. (59) can be written as

$$\langle w; S\rangle_1 = \langle \varphi^{(0)} | V | L\varphi^{(0)} \rangle + \langle L\varphi^{(0)} | V | \varphi^{(0)} \rangle$$

$$= \langle \varphi^{(0)} | VL + L^\dagger V | \varphi^{(0)} \rangle$$

$$= \langle \varphi^{(0)} | [V, L] | \varphi^{(0)} \rangle = \langle \varphi^{(0)} | [H, L] | \varphi^{(0)} \rangle \ . \tag{60}$$

Dalgarno's choice of the screening constant is such that $\langle \omega; S \rangle_1 = 0$, and therefore the corresponding hypervirial theorem is satisfied.

The satisfaction of the hypervirial theorem (58) has the interesting consequence that the wave function $\varphi^{(0)}$ is energetically stable with respect to variations of the type[11]

$$\varphi^{(0)} \longrightarrow \varphi^{(0)} + \lambda L \varphi^{(0)} \; ; \tag{61}$$

that is, the energetically optimum value of λ is zero.

Given the function F, the hypervirial operator L is determined by the equation

$$L \varphi^{(0)} = F \varphi^{(0)} \; . \tag{62}$$

In order to be anti-Hermitian and real, L must involve derivatives of odd order with respect to the coordinates. If we are not concerned with the $\langle \omega; S \rangle_j$ for which $j > 1$, it suffices to take L to be a linear function of the first derivatives with respect to the coordinates. The most general operator of this form is[11]

$$L = \sum_K \frac{f_K^{1/2}}{q^{1/2}} \frac{\partial}{\partial q_K} \left(q^{1/2} f_K^{1/2} \right) , \tag{63}$$

where q is the product of the metric scale factors of the generalized coordinates q_K and the f_K may be functions of all the q_K. Eq. (62) then reduces to a differential equation for the f_K:

$$\sum_K \frac{f_K^{1/2}}{q^{1/2}} \frac{\partial}{\partial q_K} \left(q^{1/2} f_K^{1/2} \varphi^{(0)} \right) = F \varphi^{(0)} . \tag{64}$$

Little can be said about the solution of Eq. (64) in general. However, the one-dimensional case is particularly simple, since Eq. (64) then reduces to

$$\frac{\partial f}{\partial q} + 2 \frac{\partial}{\partial q} \ln \left(q^{1/2} \varphi^{(0)} \right) = 2F , \tag{65}$$

which has the general solution

$$f = \frac{1}{q \varphi^{(0)2}} \left[2 \int q F \varphi^{(0)2} dq + C \right] . \tag{66}$$

The hypervirial operator is then obtained by substituting into the appropriate form of Eq. (63). Since $\varphi^{(0)}$ is an eigenfunction of H_o, however, it is unnecessary to find L explicitly because Eq. (58) simplifies to

$$\left\langle \varphi^{(0)} \middle| \sum_K f_K \frac{\partial V}{\partial q_K} \middle| \varphi^{(0)} \right\rangle = 0 . \tag{67}$$

For the special case of the two-electron atom, we have

$$V = \frac{1}{r_{12}} - S \left(\frac{1}{r_1} + \frac{1}{r_2} \right) , \tag{68}$$

so that

$$\frac{\partial V}{\partial r_1} = \frac{r_2 \cos \vartheta_{12} - r_1}{r_{12}^3} + \frac{S}{r_1^2} . \tag{69}$$

The function f may be determined readily for the cases discussed in Sec. III. For the property $w = \rho_1^n$ with n positive, the function F is given by Eq. (39).[12] Integration of Eq. (66) then yields the expression

$$f = \langle \rho_1^n \rangle_{0,0} \left[-\frac{n}{4}\left(\frac{1}{\rho_1^2} + \frac{2}{\rho_1} + 2\right) + 2\sum_{k=1}^{n} \frac{1}{k+1} \sum_{j=1}^{k} \frac{2^j}{(j+2)!}\, \rho_1^j \right] . \tag{70}$$

Therefore, the hypervirial operator corresponding to ρ_1^n may be constructed much more directly than would seem apparent from the discussion of Bangudu.[13]

Similarly, for $w = 1/\rho_1$, with F given by Eq. (42), we find

$$f = -\rho_1 . \tag{71}$$

Note that Eq. (67) then implies that the optimum choice of the screening parameter is such that the perturbing potential makes no contribution to the usual Clausius virial of the force.

For $w = 1/\rho_1^2$ the expression for f is somewhat more complicated. Integration of Eq. (66), with F from Eq. (44), yields

$$f = \frac{1}{\rho_1^2}\left[-\gamma - \ln 2 + 2(1-\gamma-\ln 2)\rho_1 + (3-2\gamma-2\ln 2)\rho_1^2 - \right.$$

$$\left. -2\rho_1^3 - (1+2\rho_1+2\rho_1^2)\ln \rho_1 + e^{2\rho_1} \mathrm{Ei}(-2\rho_1) \right] . \tag{72}$$

A similar expression is obtained for the case $w = \delta(\vec{\rho}_1)$.

Using Eq. (47) for F , we find

$$f = \frac{1}{2\pi\rho_1^2}\left[-\gamma - \ln 2 + 2(1-\gamma-\ln 2)\rho_1 + 2(1-\gamma-\ln 2)\rho_1^2 - \right.$$

$$\left. -2\rho_1^3 - (1+2\rho_1+2\rho_1^2)\ln\rho_1 + e^{2\rho_1}Ei(-2\rho_1)\right] . \qquad (73)$$

Example showing equivalence of Dalgarno and hypervirial methods:

The relationships discussed above may be illustrated conveniently by the following simple example: Consider the hydrogen-like one-electron atom whose Hamiltonian is

$$H_o = -\frac{1}{2}\nabla^2 - \frac{a}{r} \quad . \qquad (74)$$

The ground state eigenfunction is

$$\varphi_o = \left(\frac{a^3}{\pi}\right)^{1/2} e^{-ar} \quad , \qquad (75)$$

and the corresponding eigenvalue is $\epsilon_o = -a^2/2$. Let the atom be perturbed by a potential of the form $V = r^3 - r^2$ and suppose we wish to calculate the expectation value of the operator $W = r$.

Following the method of Dalgarno, we solve the differential equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\varphi_o^2\frac{dF}{dr}\right) = 2(W - \langle W\rangle_{o,o})\varphi_o^2 \quad , \qquad (76)$$

where $\langle W\rangle_{0,0} = 3/2a$, obtaining

$$F = \frac{1}{2a}\left(\frac{3}{a^2} - r^2\right). \tag{77}$$

The constant of integration has been fixed by the orthogonality condition $\langle F\rangle_{0,0} = 0$. The first order correction to the expectation value $\langle W\rangle$ is then

$$2\langle\varphi_0|V|F\varphi_0\rangle = \frac{9}{2a^5}\left(3 - \frac{25}{2a}\right). \tag{78}$$

This quantity is made to vanish by the choice $a = 25/6$.

The function f is determined from Eq. (66) to be

$$f = \frac{1}{a^2}\left(\frac{r^2}{2} + \frac{r}{a}\right) \tag{79}$$

and the corresponding hypervirial operator is

$$L = \frac{f^{1/2}}{r}\frac{d}{dr}\left(r f^{1/2}\right) = \frac{1}{a^2}\left[r + \frac{3}{2a} + \left(\frac{r^2}{2} + \frac{r}{a}\right)\frac{d}{dr}\right]. \tag{80}$$

It is easily verified that Eq. (65) is satisfied for this choice of L . We then have

$$\langle\varphi_0|[H, L]|\varphi_0\rangle = \langle\varphi_0|[V, L]|\varphi_0\rangle$$

$$= -\langle\varphi_0|f\frac{dV}{dr}|\varphi_0\rangle = -\frac{27}{2a^6}\left(\frac{25}{6} - a\right). \tag{81}$$

This quantity vanishes if $a = 25/6$, which is the same as the value determined by Dalgarno's criterion. Therefore, Dalgarno's method is completely equivalent to requiring that the wave function φ_o satisfy the hypervirial theorem with respect to the operator defined by Eq. (80).

V. MAXIMIZED EXPECTATION VALUES

In Sec. III it was seen that Dalgarno's method provides apparent lower bounds for the expectation values of the positive powers of the radial coordinate. We surmise that this method may give a lower bound for the expectation value of any positive definite operator W. This suggests that it might be possible to realize further improvement by maximizing the expectation value

$$\langle W \rangle_I = \frac{\langle \Psi_I | W | \Psi_I \rangle}{\langle \Psi_I | \Psi_I \rangle} \quad , \tag{82}$$

where Ψ_I is the total wave function corrected through first order.

From Eq. (7), the function Ψ_I may be written in the specific form

$$\Psi_I = \varphi^{(0,0)} + \frac{1}{Z'} \varphi^{(1,0)} + \frac{S}{Z'} \varphi^{(0,1)} \quad , \tag{83}$$

where $Z' = Z - S$. The functions $\varphi^{(1,0)}$ and $\varphi^{(0,1)}$ are solutions of the differential equations

$$(H_0 - \epsilon_0)\varphi^{(1,0)} + (V_1 - \langle V_1 \rangle_{0,0})\varphi^{(0,0)} = 0 \tag{84}$$

and

$$(H_0 - \epsilon_0)\varphi^{(0,1)} + (V_2 - \langle V_2 \rangle_{0,0})\varphi^{(0,0)} = 0 \quad , \tag{85}$$

where V_1 and V_2 are defined by Eqs. (5) and (6). Eq. (84) has been solved variationally by Scherr and Knight,[1a] who give the function $\varphi^{(1,0)}$ as a 100-term power series. Eq. (85) may be integrated directly to yield

$$\varphi^{(0,1)} = \frac{1}{\pi}(3 - \rho_1 - \rho_2)e^{-(\rho_1+\rho_2)} . \tag{86}$$

Making use of (83), the numerator of the expression (82) may be written in the explicit form

$$\langle \Psi_I | W | \Psi_I \rangle = Z'^{\alpha}\Big[\langle \varphi^{(0,0)}|w|\varphi^{(0,0)}\rangle + \frac{2}{Z'}\langle \varphi^{(0,0}|w|\varphi^{(1,0)}\rangle +$$

$$+ \frac{2S}{Z'}\langle \varphi^{(0,0)}|w|\varphi^{(0,1)}\rangle + \frac{1}{Z'^2}\langle \varphi^{(1,0)}|w|\varphi^{(1,0)}\rangle +$$

$$+ \frac{2S}{Z'^2}\langle \varphi^{(1,0)}|w|\varphi^{(0,1)}\rangle + \frac{S^2}{Z'^2}\langle \varphi^{(0,1)}|w|\varphi^{(0,1)}\rangle\Big] , \tag{87}$$

while the denominator becomes

$$\langle \Psi_I | \Psi_I \rangle = 1 + \frac{1}{Z'^2}\langle \varphi^{(1,0)}|\varphi^{(1,0)}\rangle +$$

$$+ \frac{2S}{Z'^2}\langle \varphi^{(1,0)}|\varphi^{(0,1)}\rangle + \frac{S^2}{Z'^2}\langle \varphi^{(0,1)}|\varphi^{(0,1)}\rangle . \tag{88}$$

The first order terms in the integral $\langle \Psi_I | \Psi_I \rangle$ drop out because the functions $\varphi^{(1,0)}$ and $\varphi^{(0,1)}$ are both orthogonal to $\varphi^{(0,0)}$. Using (86),

together with the results of Scherr and Knight for $\varphi^{(1,0)}$, all the matrix elements of (87) and (88) may be evaluated either analytically or by simple numerical calculations. Most of the integrals required may be taken directly from the results of Sec. III or from reference (1b). The screening parameter may then be varied to maximize the expectation value (82).

VI. RESULTS AND DISCUSSION

Some of the expectation values computed by the various methods discussed above are summarized in Tables I, II, and III for He, Li^{+}, and Be^{++}, respectively. The zeroth and first order hydrogenic ($S = 0$) values are included for comparison. The first order perturbed Hartree-Fock values included in Table I are taken from a paper by Weiss and Martin.[14]

The improvements obtained by adjusting the screening parameter are evident in all cases. Variations of S become less significant as Z increases, but the improvement is still noticeable for Be^{++}, especially for the higher powers of r_1. For all the observables listed in Tables I, II, and III, the expectation values calculated by Dalgarno's method are bounded from above by the values which are correct through sixth order.

For the positive powers of r_1, the results are improved appreciably by maximizing the expectation values calculated with the approximate eigenfunction Ψ_I of Eq. (83). For the observables $1/r_1$, $1/r_1^2$ and $\delta(\vec{r}_1)$, as might be expected, the maximization of the expectation value led to the condition $S=0$. This gives the largest possible amplitude of the wave function at the nucleus.

In the last columns of Tables I, II, and III are listed the percentages of the higher order corrections which are recovered in the best first order screening approximation. For the positive powers of r_1, more than ninety per cent of the discrepancy (with respect to the values obtained by Scherr and Knight) has been

TABLE I.

EXPECTATION VALUES OF ONE-ELECTRON OPERATORS W FOR THE HELIUM ATOM $\langle W \rangle$

W	Hydrogenic (s=0) Zeroth Order	Hydrogenic (s=0) First Order	First order energy-optimized	Dalgarno's Method	Maximized expectation value	First order perturbed H-F	Scherr-Knight sixth order	S from Dalgarno's method	S from max. expectation value	Per cent higher order terms recovered
r_1	0.75	0.89063	0.92181	0.92308	0.92663	0.9272	0.92929	0.3750	0.4173	93.1
r_1^2	0.75	1.04883	1.16080	1.16959	1.18053	1.1848	1.19234	0.3984	0.4344	91.8
r_1^3	0.9375	1.52527	1.85338	1.89416	1.92413		1.96206	0.4180	0.4517	91.3
r_1^4	1.4063	2.62793	3.57621	3.74483	3.82964		3.94435	0.4344	0.4668	91.3
r_1^5	2.4609	5.21892	8.07007	8.75358	9.01093		9.35833	0.4483	0.4796	91.6
r_1^6	4.9219	11.71671	20.8037	23.6314	24.4781			0.4602	0.4904	
r_1^7	11.074	29.30892	60.2105	72.3746	75.4014			0.4705	0.4996	
r_1^{-2}	8.0	5.82945	5.97328	5.97667			6.01740	0.2713		78.3
$\pi\,\delta(\vec{r}_1)$	8.0	5.32952	5.57389	5.61558		5.64764	5.68760	0.2225		79.9
r_1^{-1}	2.0	1.6875	1.6875	1.6875		1.6872	1.68834	0.3125		0.0

TABLE II.

EXPECTATION VALUES OF ONE-ELECTRON OPERATORS W FOR THE ION Li^+

W	$\langle W \rangle$ Hydrogenic (s=0) Zeroth Order	Hydrogenic (s=0) First Order	First order energy-optimized	Dalgarno's Method	Maximized expectation value	Scherr-Knight sixth order	S from Dalgarno's method	S from max. expectation value	Per cent higher order terms recovered
r_1	0.5	0.56250	0.57112	0.57143	0.57224	0.57277	0.3750	0.3959	94.8
r_1^2	0.333	0.42187	0.44192	0.44325	0.44477	0.44625	0.3984	0.4162	93.9
r_1^3	0.2777	0.39388	0.43187	0.43569	0.43817	0.44120	0.4180	0.4345	93.6
r_1^4	0.2777	0.44201	0.50955	0.51929	0.52348	0.52934	0.4344	0.4502	93.3
r_1^5	0.32407	0.56620	0.70360	0.72792	0.73545	0.74712	0.4483	0.4635	93.6
r_1^{-2}	18.0	14.74417	14.88800	14.89139		14.92763	0.2713		80.3
$\pi \delta(\vec{r}_1)$	27.0	20.99142	21.36000	21.42596		21.52633	0.2225		81.2
r_1^{-1}	3.0	2.6875	2.6875	2.6875		2.68793	0.3125		0.0

TABLE III

EXPECTATION VALUES OF ONE-ELECTRON OPERATORS W FOR THE ION BE^{++}

W	$\langle W \rangle$ Hydrogenic Zeroth Order	(s=0) First Order	First order energy-optimized	Dalgarno's Method	Maximized expectation value	Scherr-Knight sixth order	S from Dalgarno's method	S from max. expectation value	Per cent higher order terms recovered
r_1	0.375	0.41016	0.41367	0.41379	0.41410	0.41428	0.3750	0.3885	95.6
r_1^2	0.1875	0.22485	0.23091	0.23128	0.23169	0.23207	0.3984	0.4097	94.7
r_1^3	0.11719	0.15392	0.16241	0.16318	0.16366	0.16421	0.4180	0.4284	94.7
r_1^4	0.08789	0.12607	0.13778	0.13920	0.13978	0.14055	0.4344	0.4443	94.7
r_1^5	0.07690	0.12000	0.13677	0.13933	0.14007	0.14119	0.4483	0.4578	94.7
r_1^{-2}	32.0	27.65890	27.80272	27.80611		27.84011	0.2713		81.2
$\pi\,\delta(\vec{r}_1)$	64.0	53.31808	53.81083	53.90107		54.02992	0.2225		81.9
r_1^{-1}	4.0	3.6875	3.6875	3.6875		3.68775	0.3125		0.0

removed by varying the screening parameter in the first order function (83). In the other cases, Dalgarno's method accounts for approximately eighty per cent of the difference. The accuracy of the first order approximation increases as Z increases. However, it is interesting to note that, for a given Z, the percentage improvement is substantially constant for r_1^2 through r_1^5. Thus the expectation values of r_1^6 and r_1^7 included in Table I are probably of the same order of accuracy as the lower powers.

The values of the screening parameter determined by Dalgarno's criterion for the observables r_1^n are plotted in Fig. 1. For $n = -3$, the value plotted is the one obtained for the delta-function, $\delta(\vec{r}_1)$. For the positive powers of r_1, the screening constant is given explicitly by Eq. (41). This function increases from a value of 3/8 for $n = 1$ toward a limit of 5/8 for infinite n. For large n, the screening parameter is given approximately by the relation

$$S_n \approx \frac{5}{8} + \frac{0.519}{n} - \frac{1}{n^2} - \frac{3}{4n} \ln n \,. \qquad (89)$$

It should be pointed put that the limiting value $S_\infty = 5/8$ is different from the value $S = Z - \sqrt{|E|}$ (≈ 0.3 for He) which is obtained by requiring that the screened wave function display the correct asymptotic behavior.

The trends in the values of the screening constant obtained in the optimization procedure may be understood on the basis of a comparison of the behavior of the screened function with that of the

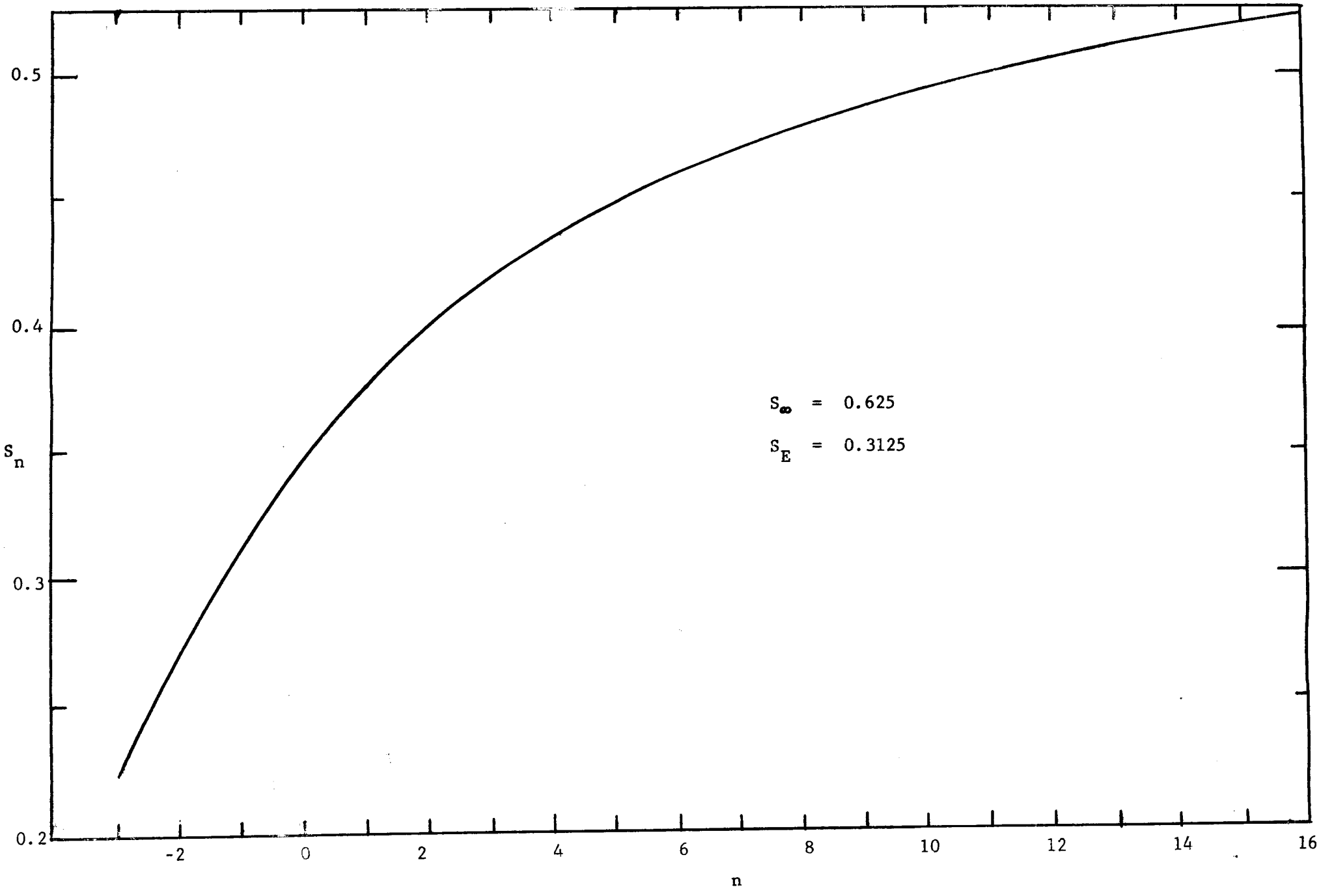

Fig. 1

FIGURE CAPTION

Fig. 1 Variation of the screening constants Sn corresponding to the observables r_1^n, as determined by Dalgarno's method. The case n = -3 corresponds to the delta-function $\delta(\vec{r}_1)$.

exact wave function. As pointed out by Dalgarno,[2] the energy-optimized function has too much of the charge density concentrated near the nucleus. The increase in the value of the screening parameter for higher powers of r_1 decreases the rate of decay of the wave function and increases the contribution from regions farther from the nucleus. For the observables $1/r_1^2$ and $\delta(\vec{r}_1)$, on the other hand, the best screening constants are less than the energy-optimized value, indicating that the amplitude of the approximate function starts out too small at the origin and falls off too slowly.

For H^-, variation of the expectation value Eq. (80) did not yield physically reasonable results. The maximization procedure led to the condition $s = 1$, corresponding to complete shielding. Dalgarno's method still produces marked improvement, as may be seen from Table IV, but the optimum screened values are appreciably smaller than the Scherr and Knight values. Moreover, the $1/Z$ expansion converges slowly when $Z = 1$, especially for the higher powers of r_1, and the errors involved in truncating at sixth order are probably quite large.

Coefficients of the $1/Z$ expansions of expectation values in the Dalgarno approximation, Eqs. (53) and (54), are given in Table V. The corresponding values obtained by Scherr and Knight are included for comparison. The screening constants are given by Eq. (51). Total expectation values obtained by Dalgarno's method for the case $Z = 2$ are listed in the third column, together with the values correct through sixth order. In general, the best results are obtained for operators involving only the radial coordinate r_1,

TABLE IV

EXPECTATION VALUES OF ONE-ELECTRON OPERATORS W FOR THE ION H^-

$\langle W \rangle$

W	Hydrogenic (s=0) Zeroth Order	Hydrogenic (s=0) First Order	First order energy-optimized	Dalgarno's Method	Scherr-Knight sixth order	Per cent higher order terms recovered
r_1	1.5	2.06250	2.38017	2.40000	2.54360	70.2
r_1^2	3.0	5.39062	7.93388	8.29010	9.50684	70.4
r_1^3	7.5	16.9043	33.7026	38.0384	45.9546	72.8
r_1^4	22.5	61.5937	172.130	219.820	264.521	78.0
r_1^5	78.75	255.260	1019.05	1540.50	1726.92	87.3
r_1^{-2}	2.0	0.91472	1.05856	1.06195	1.11660	72.9
$\pi\delta(\vec{r}_1)$	1.0	0.33238	0.45250	0.46992	0.51478	75.4
r_1^{-1}	1.0	0.6875	0.6875	0.6875	0.68818	0.0

TABLE V

COEFFICIENTS OF THE 1/Z EXPANSIONS OF VARIOUS EXPECTATION VALUES AS DETERMINED BY DALGARNO'S METHOD. THE VALUES OBTAINED BY SCHERR AND KNIGHT ARE UNDERLINED

W	Dalgarno Screening Constant	$\langle W \rangle_{Z=2}$	$\langle w \rangle_{0,0}$	$\langle w \rangle_{1,0}$	$\langle w \rangle_{2,0}$	$\langle w \rangle_{3,0}$	$\langle w \rangle_{4,0}$	$\langle w \rangle_{5,0}$	$\langle w \rangle_{6,0}$
$r_1^{-1} r_2^{-1}$	0.349	2.73	1.0	-0.698	0.122	...	...	...	...
		<u>2.71</u>			<u>0.107</u>	<u>-0.00199</u>	<u>0.00821</u>	<u>-0.00498</u>	<u>-0.00320</u>
r_1^{-2}	0.271	5.98	2.0	-1.09	0.147	...	...	...	...
		<u>6.02</u>			<u>0.175</u>	<u>0.0268</u>	<u>0.00001</u>	<u>0.00010</u>	<u>0.00049</u>
r_1^{-1}	0.313	1.69	1.0	-0.313	...	...	...	...	...
		<u>1.69</u>			<u>-1×10^{-9}</u>	<u>0.00435</u>	<u>-0.00089</u>	<u>-0.00155</u>	<u>-0.00123</u>
r_1	0.375	0.923	1.5	0.563	0.211	0.0791	0.0297	0.0111	0.00417
		<u>0.929</u>			<u>0.233</u>	<u>0.106</u>	<u>0.0625</u>	<u>0.0448</u>	<u>0.0347</u>
r_1^2	0.398	1.17	3.0	2.39	1.43	0.759	0.378	0.181	0.0840
		<u>1.19</u>			<u>1.55</u>	<u>0.978</u>	<u>0.672</u>	<u>0.508</u>	<u>0.408</u>
r_1^3	0.418	1.89	7.5	9.40	7.86	5.48	3.43	2.01	1.12
		<u>1.96</u>			<u>8.41</u>	<u>6.78</u>	<u>5.45</u>	<u>4.53</u>	<u>3.87</u>

TABLE V (cont'd)

W	Dalgarno Screening Constant	$\langle W \rangle_{Z=2}$	$\langle w \rangle_{0,0}$	$\langle w \rangle_{1,0}$	$\langle w \rangle_{2,0}$	$\langle w \rangle_{3,0}$	$\langle w \rangle_{4,0}$	$\langle w \rangle_{5,0}$	$\langle w \rangle_{6,0}$
r_1^4	0.434	3.74	23.5	39.1	42.5	36.9	28.0	19.5	12.7
		3.94			45.0	44.2	41.1	37.8	34.9
r_1^5	0.448	8.75	78.8	177.	237	248	223	180	134
		9.36			249	290	307	313	312
r_{12}^{-2}	0.543	1.42	0.667	-0.724	0.197	...	...	...	...
		1.46			0.269	-0.0419	-0.00571	-0.00165	-0.00139
r_{12}^{-1}	0.505	0.935	0.625	-0.315	...	...	...	...	...
		0.946			0.0261	-0.00355	-0.00518	-0.00369	-0.00261
r_{12}	0.471	1.43	2.19	1.03	0.485	0.228	0.107	0.0506	0.0238
		1.42			0.424	0.194	0.115	0.0827	0.0645
r_{12}^2	0.462	2.54	6.0	5.54	3.83	2.36	1.36	0.754	0.406
		2.51			3.56	2.13	1.38	1.01	0.806
$r_1^{-1} r_{12}^{-1}$	0.403	1.91	0.75	-0.604	0.121	...	...	...	...
		1.92			0.134	-0.00677	-0.00692	-0.00333	-0.00214

TABLE V (cont'd)

W	Dalgarno Screening Constant	$\langle W \rangle_{Z=2}$	$\langle w \rangle_{0,0}$	$\langle w \rangle_{1,0}$	$\langle w \rangle_{2,0}$	$\langle w \rangle_{3,0}$	$\langle w \rangle_{4,0}$	$\langle w \rangle_{5,0}$	$\langle w \rangle_{6,0}$
$r_1^2 r_{12}^{-1}$	0.249	0.584	1.31	-0.327	0.0813	-0.0203	0.00504	-0.00126	0.00031
		0.607			0.187	0.0958	0.0604	0.0440	0.0341
$r_1^3 r_{12}^{-1}$	0.344	1.02	2.79	1.92	0.987	0.452	0.194	0.0801	0.0321
		1.06			1.33	0.897	0.647	0.501	0.406
$r_1^4 r_{12}^{-1}$	0.386	1.71	7.21	8.34	6.43	4.13	2.39	1.29	0.663
		1.83			7.63	6.35	5.26	4.45	3.84
$r_1^5 r_{12}^{-1}$	0.413	3.47	22.0	36.4	37.5	31.0	22.4	14.8	9.16
		3.76			42.1	42.1	39.8	37.1	34.5
$\frac{r_1 r_2 \cos\vartheta_{12}}{r_{12}}$	-0.860	0.0765	0.219	-0.188	0.162	-0.139	0.120	-0.103	0.00884
		0.0593			-0.0252	-0.00122	0.00299	0.00266	0.00183
$\frac{r_1^2 r_2 \cos\vartheta_{12}}{r_{12}}$	-0.301	0.0723	0.383	-0.230	0.104	-0.0417	0.0157	-0.00566	0.00199
		0.0651			-0.0109	-0.0373	-0.00463	0.00482	0.00571
$\frac{r_1^3 r_2 \cos\vartheta_{12}}{r_{12}}$	-0.103	0.0869	0.809	-0.250	0.0514	-0.00883	0.00136	-0.00020	0.00003
		0.0729			-0.301	-0.174	-0.0586	-0.00082	0.0184

TABLE V (cont'd)

W	Dalgarno Screening Constant	$\langle W \rangle_{Z=2}$	$\langle w \rangle_{0,0}$	$\langle w \rangle_{1,0}$	$\langle w \rangle_{2,0}$	$\langle w \rangle_{3,0}$	$\langle w \rangle_{4,0}$	$\langle w \rangle_{5,0}$	$\langle w \rangle_{6,0}$
$\frac{r_1^2 r_2^2 \cos\vartheta_{12}}{r_{12}}$	-0.122	0.0757	0.723	-0.264	0.0643	-0.0131	0.00239	-0.00041	0.00007
		0.0619			-0.286	-0.162	-0.0570	-0.00585	0.0107
$\pi\,\delta(\vec{r}_1)$	0.223	5.62	1.0	-0.668	0.149	-0.0110	...	...	...
		5.69			0.177	0.00435	-0.00107	0.00124	0.00096
$\pi\,\delta(\vec{r}_{12})$	0.649	0.309	0.125	-0.243	0.297	-0.0340	...	...	...
		0.334			0.184	-0.0668	0.00932	0.00051	-0.00019

but there are some surprising exceptions. In particular, the $1/Z$ expansions of the expectation values of r_{12} and r_{12}^2 are reproduced very well by Dalgarno's method. It is interesting to note that, because of the wide variation of the importance of the higher terms, there is relatively little correlation between the overall accuracy of Dalgarno's method and its success in reproducing the individual coefficients of the $1/Z$ expansions. The poorest results are obtained for the operators containing the factor $r_{12}^{-1}\cos\vartheta_{12}$. Here the screening constants obtained by Dalgarno's criterion are negative and the expectation values are significantly different from those calculated by Scherr and Knight. The inadequacy of the method in this case is probably due to the spherical symmetry of the zeroth order function. For operators whose only angular dependence is in the factor $\cos\vartheta_{12}$, the coefficient $\langle w\rangle_{0,0}$ vanishes and Dalgarno's method cannot be used at all. On the basis of our results, therefore, it seems clear that Dalgarno's criterion should only be applied to the calculation of properties associated with positive definite operators.

In general, the screening constants determined by the Dalgarno criterion differ appreciably from the energy-optimized value. Therefore, the improvements in the expectation values of the various observables are obtained at the expense of the total energy of the atom. The magnitude of this energy sacrifice is a matter of interest. Energies calculated through first order with the values of S determined from Dalgarno's criterion by optimizing $\langle r_1\rangle$ through $\langle r_1^7\rangle$ are listed in Table VI, together with the results

TABLE VI

TOTAL ENERGIES ACCURATE THROUGH FIRST ORDER AS COMPUTED WITH SCREENING CONSTANTS DETERMINED BY DALGARNO'S METHOD. THE ENERGY SCREENING CONSTANTS ARE THE SAME AS FOR r_1^{-1}.

W	H^-			He		Li^+		Be^{++}	
	s	-E(s)	Per cent change	-E(s)	Per cent change	-E(s)	Per cent change	-E(s)	Per cent change
r_1^{-1}	0.3125	0.47266	...	2.84766	...	7.22266	...	13.59766	...
r_1	0.3750	0.46875	0.83	2.84375	0.14	7.21875	0.054	13.59375	0.029
r_1^2	0.3984	0.46528	1.56	2.84028	0.26	7.21528	0.10	13.59028	0.054
r_1^3	0.4180	0.46153	2.36	2.83653	0.39	7.21153	0.15	13.58653	0.082
r_1^4	0.4344	0.45780	3.14	2.83280	0.52	7.20780	0.21	13.58280	0.11
r_1^5	0.4483	0.45421	3.90	2.82921	0.65	7.20421	0.26	13.57921	0.14
r_1^6	0.4602	0.45084	4.62	2.82584	0.77	7.20084	0.30	13.57584	0.16
r_1^7	0.4705	0.44769	5.28	2.82269	0.88	7.19769	0.35	13.57269	0.18

obtained by minimizing the expectation value of the Hamiltonian. The minimum energies in the screening approximation differ from the most exact values[1a] by 10.4 per cent for H^-, 1.9 per cent for He, 0.8 per cent for Li^+, and 0.4 per cent for Be^{++}. Except for H^-, the energy loss due to the variations of S is less than one per cent in all cases. As Z increases, of course, changes in the screening constant become less important. It should be noted that the energy loss in the most unfavorable case shown in Table VI is only about one-half the error of the best energy in the screening approximation.

REFERENCES

1. (a) C. W. Scherr and R. E. Knight, Rev. Mod. Phys., 35, 436 (1963).
(b) C. W. Scherr and R. E. Knight, J. Chem. Phys. 40, 3034 (1964).
2. A. Dalgarno and A. L. Stewart, Proc. Roy. Soc., A257, 534 (1960).
3. P. D. Robinson, Private communication.
4. L. Pauling, Proc. Rpy. Soc., A114, 181 (1927).
5. L. Pauling and J. Sherman, Zeit. f. Kristallographie, 81, 1 (1932).
6. J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, "Advances in Quantum Chemistry", (Edited by P. O. Löwdin, Academic Press, New York, 1964), Chap. 00.
7. H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", (John Wiley and Sons, New York, 1944), p. 104.
8. A. Dalgarno and A. L. Stewart, Proc. Roy. Soc. A247, 245 (1958).
9. S. L. Gordon, University of Wisconsin Theoretical Chemistry Institute Report No. 18 (1963).
10. J. O. Hirschfelder, J. Chem. Phys. 33, 1462 (1960).
11. S. T. Epstein and J. O. Hirschfelder, Phys. Rev., 123, 1495 (1961).
12. Instead of using f as determined by the condition $L\varphi^{(0)} = F\varphi^{(0)}$, Gordon specified his screening constants by requiring that $f = \rho_1^n$. He computed expectation values of positive powers of the radial coordinate for several choices of n . His results were somewhat better than those utilizing the energy-optimized screening constant, the best overall improvement being obtained by using $f = \rho_1^2$. However, the results were not as good as those he obtained by using Dalgarno's method.

REFERENCES (cont'd)

13. E. Adeniyi Bangudu, Progress Report, Wave Mechanics Group, Mathematical Institute, Oxford, 10, 22 (1964).

14. A. W. Weiss and J. B. Martin, Phys. Rev., 132, 2118 (1963). The first order correction to the Hartree-Fock wave function of helium is obtained by a variational procedure.