large energy range. Although it is unfortunate that the parameters in the Bethe formula have not been calculated from theory for any of the gases investigated here, the formula appears to be a reliable tool for interpolating between and extrapolating beyond measured values of specific primary ionization at energies in excess of a few kev.

At very low energies, there is a systematic departure of the theory from the experimental results, which must be attributed to the weakness of the present theory. The only cases where the Bethe formula extrapolations of the present data are inconsistent are the experimental results of others in the neighborhoods of $p/Mc=0.05$ and $p/Mc=19$ occur in the case of He, where the low energy data of Smith[2] fall below the theoretical curve, and in the case of A where the cosmic-ray point of Cosyns[5] lies above the curve. The decision as to whether these discrepancies are attributable to the theory or to the experimental technique is difficult to make at the present time.

The data obtained in the present investigation, in addition to serving as a useful guide toward further development of the theory of ionization, should be of value both in the design of low efficiency G-M counters and in the analysis of cloud-chamber photographs containing the tracks of fast particles.

Measurements of the specific primary ionization of several other simple gases and of some of the complex organic vapors utilized in G-M counters will be carried out in the near future.

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Two-Electron Self-Consistent Field

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Stevenson's extension of the Hartree self-consistent field (s.c.f.) method, to take some account of polarization interaction between two outer electrons, is worked out numerically, up to a point, for H^-. The two-electron wave function is a product of two one-electron radial functions and a function X of the angle between the two radii. Several integrals must be calculated and a boundary value problem for X must be solved prior to the stage of ordinary Hartree calculations. These fundamental computations are made here, but the routine solution of the radial Hartree equations has been omitted; instead the Stevenson corrections to the total energy are estimated by perturbation methods. These corrections seem just about large enough to yield an electron affinity for H^- (something not achieved by s.c.f. or variation methods without polarization). However, a good deal of labor is involved beyond that required for s.c.f. solutions, and it is not certain that this particular method of including polarization effects is to be preferred to a combination of variation and s.c.f. calculations.

INTRODUCTION

ABOUT 15 years ago Stevenson published an extension of the Hartree self-consistent field (s.c.f.) equations, designed to handle cases of two electrons outside closed shells, including allowance for spatial symmetry properties and mutual polarization energy.[1] So far as the present author knows, no calculations have been carried out by this method, save for some approximate ones reported by Stevenson himself in a later paper.[2]

In view of continuing interest in such atomic structures (mainly in the form of loosely bound negative ions—specific references appear below), it seemed worth while to work out one trial example. The aim is to assess the difficulties and the gains of the Stevenson method, in comparison with both conventional s.c.f. and variation procedures. For such a trial the H^- ion seems ideally suited. Its properties have importance in solar spectroscopy, its electron affinity and wave functions have been found with considerable precision by a lengthy variational method, and yet neither the s.c.f. nor the simplest variational calculation[3] yield a positive electron affinity.

Stevenson's paper gives equations applicable to any configuration of the two electrons, but for H^- we shall consider only the simple case of two $1s$ orbits, without exchange. The pertinent equations are (pp. 596–598 of reference 1)

$$\chi_i''(r_i)+[\epsilon_i+2V(r_i)+C/r_i^2-2U_i(r_i)]\chi_i(r_i)=0, \quad (i=1,\,2), \tag{1}$$

$$\frac{d}{dx}[(1-x^2)X'(x)]+[\epsilon_3-U_3(x)]X(x)=0, \tag{2}$$

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[1] A. F. Stevenson, Proc. Roy. Soc. (London) **A160**, 588 (1937).

[2] A. F. Stevenson, Phys. Rev. **56**, 586 (1939).

[3] That is, the one using spherically symmetrical hydrogen-like wave functions.

$$C=\int_{-1}^{1}[U_3(x)-\epsilon_3]X^2(x)dx, \tag{3}$$

$$U_1(r_1)=\int_{-1}^{1}dx\int_0^\infty dr_2(1/r_{12})\chi_2^2(r_2)X^2(x), \tag{4}$$

[and similarly for $U_2(r_2)$],

$$U_3(x)=\frac{\int_0^\infty\int_0^\infty dr_1dr_2\chi_1^2(r_1)\chi_2^2(r_2)/r_{12}}{\int_0^\infty dr[\chi_1^2(r)+\chi_2^2(r)]/r^2}. \tag{5}$$

[The numerator of Eq. (5) occurs often in atomic theory.] The notation is that of Stevenson, except that $\chi(r)$ replaces his $P(r)$. The wave function assumed for the two electrons is $(1/r_1)\chi_1(r_1)(1/r_2)\chi_2(r_2)X(x)$. $\chi(r)$ is the "Hartree radial wave function"; x is the cosine of the angle θ between the radii r_1 and r_2. "1" and "2" refer to the respective electrons, which are indistinguishable (both being 1s) in our example. It is assumed that χ_1, χ_2, and X are individually normalized.

In principle the calculations are straightforward. Starting with an assumed pair of Hartree wave functions χ_1, χ_2, one evaluates $U_3(x)$ from Eq. (5), solves the eigenvalue Eq. (2) for X, evaluates C, U_1, and U_2, and finally solves the two equations contained in Eq. (1) exactly as in s.c.f. problems. For H^-, $V(r)$ is merely the negative of the Coulomb potential of the nucleus.[4] Then the whole chain of calculations can be repeated until full self-consistency is attained.

Stevenson shows (p. 603 of reference 1) that the total energy E in this special case of two equivalent electrons is given by

$$E=\epsilon_1+\epsilon_2-2\int_0^\infty U_1(r)\chi_1^2(r)dr. \tag{6}$$

The process of starting numerical integration in Eqs. (1) will be a little more troublesome than in the conventional Hartree calculation, because the term in C introduces a nonintegral power of r into the approximating polynomial representation of $\chi(r)$. However, the main difficulties lie earlier in the chain of calculations.

EVALUATION OF $U_3(x)$

The obvious way to begin evaluating $U_3(x)$ in Eq. (5) is to expand $1/r_{12}$ in the usual series,

$$1/r_{12}=\sum_{l=0}^{\infty}(r_a^l/r_b^{l+1})P_l(x), \tag{7}$$

where r_a is the lesser and r_b the greater of the pair r_1, r_2 and $P_l(x)$ is the Legendre polynomial. If the original values of χ_1, χ_2 are tabular (e.g., from conventional s.c.f. calculations in which no account is taken of x), all the ensuing double integrations are numerical and very tedious; even worse, a great many are required because the resulting series is oscillating and very slowly convergent. Indeed, at least 30 terms may be needed—clearly an impractical venture. If instead the χ's are taken to be in the form r^je^{-ar}, the coefficients of $P_l(x)$ [after substitution of Eq. (7) into Eq. (5)] can be computed in closed form. Since any wave function can be expanded[5] in a sum of terms $r^j\exp(-a_jr)$, this procedure can be applied even to tabular wave functions. In the present paper only the first approximation is carried out, with the χ's taken to be normalized hydrogenic functions,

$$\chi(r)=(\alpha^3/2)^{\frac{1}{2}}re^{-\alpha r/2}. \tag{8}$$

The quantity α was chosen as 1.6, a value suggested by examination of the simple variational calculation and various much more precise results.[6] This evaluation of U_3 is the heart of whatever practicality the whole method may have and so merits a brief description.

After Eqs. (7) and (8) are substituted into Eq. (5), $U_3(x)$ can be written as follows:

$$U_3(x)=(4\alpha)^{-1}\sum_{l=0}^{\infty}(A_l+B_l)P_l(x), \tag{9}$$

wherein

$$A_l=\int_0^\infty y^{l+2}e^{-y}\left[\int_y^\infty x^{-l+1}e^{-x}dx\right]dy \tag{10}$$

and

$$B_l=\int_0^\infty y^{-l+1}e^{-y}\left[\int_0^y x^{l+2}e^{-x}dx\right]dy. \tag{11}$$

For x near -1 (θ near 180°, or the two electrons on opposite sides of the nucleus) a binomial expansion of $1/r_{12}$ in powers of x leads to a series expression for $U_3(x)$, valid to about $x=-0.4$. Outside this range the first few A's and B's can be evaluated by direct integration, but for values of l above 2 exponential integrals appear. There is a method by which either A_l or B_l can be found in general;[7] moreover, this same method shows that $A_l=B_l$ always.

In the rigorous calculation of A_l, Eq. (10) is altered by the insertion of a parameter β, which eventually is to approach unity, and by generalizing the exponents,

$$I_{n,k}(\beta)=\int_0^\infty y^ne^{-y}\left[\int_y^\infty x^{-k}e^{-\beta x}dx\right]dy. \tag{12}$$

Now $I_{n,k}(\beta)$ evidently satisfies a recursion formula

$$dI_{n,k}(\beta)/d\beta=-I_{n,k-1}(\beta). \tag{13}$$

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[4] For an atom or ion with inner shells, conventional s.c.f. calculations would be made for the inner electrons; $V(r)$ would then include the spherically symmetrical shielding due to these inner shells.

[5] J. C. Slater, Phys. Rev. **42**, 33 (1932).

[6] For a list of references, see S. Chandrasekhar, Revs. Modern Phys. **16**, 301 (1944).

[7] The author is indebted to his colleague Dr. David Mintzer for pointing this out.

Also, as $\beta \rightarrow 0$ we have, for $n > k$,

$$I_{n,k}(\beta) \xrightarrow[\beta\rightarrow 0]{} (k-1)^{-1}(n+1-k)!. \qquad (14)$$

Moreover, as $\beta \rightarrow \infty$,

$$I_{n,k}(\beta) \xrightarrow[\beta\rightarrow\infty]{} 0. \qquad (14a)$$

Equation (14) cannot be used for $k=1$ or zero, because a divergent integral is involved; however, Eq. (14a) serves in its place.

The general procedure hereafter is to name the desired l value, compute the associated n and k, get $I_{n,0}(\beta)$ by direct integration of Eq. (12) (over x and y), and then build up to $I_{n,k}(\beta)$ by repeated integration (over β) of Eq. (13); the constant of integration at each step is found from Eq. (14) or Eq. (14a).

The final result can be expressed in closed form:

$$A_0 = B_0 = \tfrac{5}{8}; \quad A_1 = B_1 = \tfrac{3}{8};$$

$$A_l = B_l = (l-1)(l)(l+1)(l+2) \times\left[-\ln 2 + 1 - \tfrac{1}{2} + \cdots + (-1)^{l-1}\frac{1}{l-2}\right] + (-1)^l \cdot \left[\frac{(2l^2+3l+2)(l+2)}{4} + \frac{3}{8}\right]. \qquad (15)$$

With this formula, Eq. (9), a table of Legendre polynomials[8] to order 32, and a desk calculator, a few values of $U_3(x)$ were computed. From $x=-1$ to $x \approx -0.4$, $U_3(x)$ can be found easily by binomial expansion of $1/r_{12}$; the method of Eq. (15) works—with some difficulties of oscillating convergence toward the end—to $x \approx +0.95$. Thereafter $U_3(x)$, which is a smooth monotone rising function as x increases, was approximated by the form

$$U_3(x) = K(1-x)^{-s}, \qquad (16)$$

where K and s (the latter approximating $\frac{1}{4}$) were fitted to the preceding part of the curve. It can be argued from the electrostatic analog—two charged wires making an acute angle—that U_3 should diverge in roughly this fashion as $x \rightarrow +1$. Moreover, later calculations show that the precise form of U_3 is unimportant in this small region, provided it does not diverge too fast.

Tabular values of $U_3(x)$ were read from a graph of the computed values and were then smoothed numerically.

CALCULATION OF $X(x)$

The next step—and the only other one we shall describe in any detail—is the solution of the eigenvalue problem in Eq. (2). The boundary conditions set by Stevenson are that X be finite and without a node in the closed x interval -1 to $+1$.

Equation (2) can be rewritten in integro-differential form:

$$dX/dx = X' = (1-x^2)^{-1}\int_{-1}^{x} [U_3(\xi) - \epsilon_3]X(\xi)d\xi. \qquad (17)$$

If X is to be bounded over the whole interval, X' cannot diverge as fast as $(1-x^2)^{-1}$ at $x=+1$, and therefore

$$\int_{-1}^{1} [U_3(\xi) - \epsilon_3]X(\xi)d\xi = 0. \qquad (18)$$

In a first approximation we take X as unity over the whole range and find ϵ_3 from numerical integration of Eq. (18) (U_3 being known in tabular form). Then Eq. (17) yields X' (except at $x=-1$) and numerical integration of X' determines X (the partial integrals of Eq. (18) can be used in finding X', of course). Once more a value of ϵ_3 is found, with X now varying; then a new table of X' and a new X are found. At each stage, once ϵ is known we start the integration of X' by power series solution, since $U_3(x)$ is known as far as $x=-0.4$ in series form. X is nearly constant for x near -1; it decreases slowly and monotonically as x increases, and then hooks down abruptly—though not very far—as x goes to $+1$. Because of this behavior it is well to set $X' = -d(1-X)/dx$ and integrate to find $(1-X)$.

The Milne method[9] was used for the numerical integrations, over the range $x=-0.4$ to $x=+0.96$, in steps $\Delta x = 0.08$. In the final interval $0.96 \leq x \leq 1$, two methods were tried: insertion into Eq. (17) of U_3 as given for Eq. (16), for analytic solution; and numerical integration over much smaller x intervals (0.005), with Eq. (16) used only to tabulate $U_3(x)$. The last step of the numerical integration had to be made with an "open" integration formula, since U_3 and X' diverge weakly. It was found that both methods gave closely similar results, provided a many-term integration formula was used. The numerical method is easier, on the whole.

Detailed tabulation of $U_3(x)$, $X(x)$, ϵ, etc., is not worth while. Table I is included, merely to give an idea of the functional behavior of these quantities.

The calculation converges very rapidly, e.g., the third and fourth trial values of ϵ_3 differ by less than 1 in 4000.

The final X, found by interpolation between the last two trials, is then normalized.

TABLE I. Illustrative numerical results for H^-.

x	-1	-0.4	0	0.48	0.88	0.96	0.98	$+1$
$U_3(x)$	0.1250	0.1485	0.1704	0.2184	0.3481	0.4723	0.5726	∞
$X(x)$	1.0000	0.9772	0.9589	0.9308	0.8945	0.8819	0.8774	0.8688

$\int_{-1}^{1} X^2 dx = 1.7964$, $\epsilon_3 = 0.1939$, $C = -0.00270$, $\langle x \rangle = -0.03943$, $\langle x^2 \rangle = 0.3344$.

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[8] H. Tallqvist, Acta Soc. Sci. Fennicae A2, 11 (1938).

[9] See, e.g., Bennett, Milne, Bateman, Bull. Natl. Research Council (U. S.) No. 92, 76 (1933).

EVALUATION OF $U(r)$

It is only a matter of numerical quadratures thereafter to find C [Eq. (3)] and the averages

$$\langle P_l(x)\rangle=\int_{-1}^{1} X^2(x)P_l(x)dx, \qquad (19)$$

which are needed for computation of $U_1(r)$ [Eq. (4)]. To avoid getting C as the small difference of two large quantities, it is better to substitute from Eq. (2) for the integrand of Eq. (3) and then integrate by parts, before using numerical methods.

$U_1(r_1)$, or the identical $U_2(r_2)$, is found by expanding $1/r_{12}$ in Eq. (4) according to Eq. (7) and carrying out the integrations over x and r_2 (or r_1). The integrations for $l=0$ and 1 are easy; the exponential integral enters at $l=2$, but this is no longer a bother because any further steps—the integration of Eqs. (1) in particular—must be done numerically, in general.

The first of these terms in $U(r)$, that for $l=0$, is the spherically averaged potential energy of interaction between the two electrons; such an average appears both in the conventional s.c.f. method and in the simplest variational calculation.

The next term, with $l=1$, should be the first and the most important new correction. It includes $\langle P_1(x)\rangle$, or $\langle x\rangle$, and is a consequence of electron polarization. Because the electrons tend to repel each other to opposite sides of the nucleus, their energy of interaction is decreased. (The average of x or $\cos\theta$ would be zero, with $\theta=90°$, in a spherically symmetrical electron distribution.) As Thaler has showed[10] in his calculation of the electron affinity of Na^-, this asymmetry of the electron positions gives an energy correction which is close to that computed classically for point electrons located at the maxima of the radial wave functions. Accordingly, the size of $\langle x\rangle$ gives an early indication of the importance of such corrections. In this calculation for H^-, $\langle x\rangle=-0.0394$, indicating an average θ of about 92°.

ESTIMATE OF ENERGY CORRECTIONS

Given complete tabular values of the quantities mentioned so far, integration of Eqs. (1) is merely a Hartree type of calculation, though slightly more troublesome because of its starting values. This integration was not carried out, because it was obvious by this stage that a fully self-consistent evaluation of the H^- wave functions and energy would be hopelessly lengthy without the aid of a large computing machine. It is possible, however, with little additional work to make a fairly good estimate of the importance of Stevenson's corrections for H^-, as will now be seen.

The two "new" terms in Eq. (1) are C/r^2 and parts of $-2U_1(r)$ (those parts including $\langle P_1(x)\rangle$, $\langle P_2(x)\rangle$, etc.). First-order perturbation theory shows that the energy contributions of these new terms can be found fairly accurately by averaging them over $\chi^2(r)$. Since χ has a simple analytical form, this average or integral can be found quite easily for $\langle P_1(x)\rangle$. Higher terms involve integrals like those in Eqs. (10) and (11) and can be computed similarly.

When $1/r_{12}$ in Eq. (4) is expanded in Legendre polynomials, the quantity $-2U_1(r)$ becomes

$$-2U_1(r)=-2[U(r)]_0\langle P_0(x)\rangle -2[U(r)]_1\langle P_1(x)\rangle+\cdots, \qquad (20)$$

with

$$-2[U(r)]_0=(2/r)(1-e^{-\alpha r}-\alpha e^{-\alpha r}) \qquad (21)$$

and

$$-2[U(r)]_1=3\langle x\rangle[-\alpha e^{-\alpha r}-(2/r)e^{-\alpha r} +(2/\alpha r^2)(1-e^{-\alpha r})]. \qquad (22)$$

When C/r^2 and these two parts of $U(r)$ are averaged over χ^2, the following results emerge:

$$\int_0^\infty (C/r^2)\chi^2(r)dr=\tfrac{1}{2}\alpha^2C; \qquad (23)$$

$$-2\int_0^\infty [U(r)]_0\chi^2(r)dr=-5\alpha/8; \qquad (24)$$

$$-2\int_0^\infty [U(r)]_1\chi^2(r)dr=-3\alpha\langle x\rangle/8. \qquad (25)$$

The numerical values of these, after insertion of C, α, and $\langle x\rangle$ values, are, respectively, -0.00346, -1, $+0.02366$. (The energy unit is the ionization energy of hydrogen.) The first and third of these are the "new" contributions, as has been explained above.

Next we try to estimate ϵ of Eq. (1). If the terms in C and U are deleted, the problem becomes that of the ordinary hydrogen atom, with a contribution to ϵ of -1 unit. Next, from Eq. (24), the $[U]_0$ term contributes $+1$, the C term of Eq. (23) adds 0.00346, and the $[U]_1$ term in Eq. (25) subtracts 0.02366. Therefore ϵ_1 (or ϵ_2) should be given approximately by

$$\epsilon\approx-1+1+0.00346-0.02366. \qquad (26)$$

According to Eq. (6), the total energy is given (to the same approximation) by

$$E=2-5\alpha/8+0.02366. \qquad (27)$$

Therefore we have

$$E\approx-2+2+0.0069-0.0473-1+0.0237, \qquad (28)$$

or

$$E\approx-1.0168. \qquad (29)$$

Since the hydrogen atom alone has an energy E of -1 unit, a positive electron affinity (binding effect) of about 0.017 atomic unit or 0.23 electron volt is implied (the best theoretical value[6] is about 0.75 electron volt).

It is worth mentioning that the main "new" contribution, $-3\alpha\langle x\rangle/8$, is nearly independent of α because $-\langle x\rangle$ is roughly inversely proportional to α.

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[10] R. M. Thaler, Phys. Rev. **83**, 131 (1951).

Of course this calculation is not to be trusted in detail; it merely establishes orders of magnitude. In contrast, the simplest variational calculation for H^-—which includes a term equivalent to ours in $[U]_0$ but not those in C and $[U]_1$—leads to an energy value of $-121/128$ atomic unit, with a "negative electron affinity" (no binding—instability) of 0.055 atomic unit. The variation method should yield an approximation to the true energy, not to the Hartree parameter ϵ. Therefore we expect the Stevenson correction to comprise the term in C [Eq. (23)] and that in α [Eq. (25)]. The net value of these terms is roughly 0.020 atomic unit, which is less than half the amount needed to produce a positive electron affinity.

The corrections represented by $-2[U]_2\langle P_2(x)\rangle$ can be mentioned briefly. $[U]_2$ can be evaluated by the method applied to Eq. (10). $P_2(x)$ is $\frac{1}{2}(3x^2-1)$, and so $\langle P_2(x)\rangle$ is known once $\langle x^2\rangle$ is found. The whole term $2[U]_2\langle P_2(x)\rangle$ is of magnitude 0.00066 atomic unit or about 0.009 electron volt, a negligible quantity in these approximate calculations. The small size of this correction is due jointly to U and P being small, which makes it seem reasonable to ignore all terms in higher l.

CONCLUSIONS

Two general conclusions can be drawn from this test of the Stevenson method. (1) The method involves considerable additional labor, with respect to conventional s.c.f. procedures. To be sure, much of this extra work can be carried out quite readily on a large computing machine; moreover (as will be detailed below), by no means all of it need be repeated at each stage of successive attempts to reach self-consistency. (2) It is doubtful whether this method yields a worth-while improvement in energy (and, by implication, in wave functions). To be sure, it is better than ordinary s.c.f. processes, but so may be a rather simple extension of the variation method.[11] Furthermore, Thaler[10] has shown that the s.c.f. procedure for inner shells and variation procedures for the outermost one can be combined to predict a strong electron affinity for Na^- which the s.c.f. method did not show.

Finally, a few remarks can be made for the guidance of a hypothetical future calculation. The $\chi(r)$ to be used for calculation of U_3 [Eq. (5)] can always be written as a sum of terms $r^j \exp(-a_j r)$, as noted earlier, and so at the worst U_3 would be a sum of series each similar to that shown in Eq. (9).[12] Since α (or a_j) appears only as an external factor in Eq. (9), a good deal of calculation need not be repeated in later stages. The evaluations of A_l from Eq. (15) and so of the separate series for U_3 are presumably straightforward for an automatic machine. Equations (18) and (17) are easy to solve for ϵ and X; the smooth slow variation of U_3 and X allows use of relatively long integration intervals, as mentioned earlier. When $U_3(x)$ is multiplied by a factor $(1+k)$, with k a constant of magnitude less than unity, both ϵ and $(1-X)$ change by factors approximating $(1+k)$. It is not hard to derive formulas giving $\Delta\epsilon$ and $\Delta(1-X)$ quite simply, once complete solutions for two values of k are available. Indeed the numerical values quoted here were found by just such a method, from an earlier trial of H^- with $\alpha=2$ and one of He with $\alpha=4$. Incidentally, the results for He showed that $-3\alpha\langle x\rangle/8$ [Eq. (25)] is 0.02389, in good agreement with Stevenson's estimate.[2]

Later calculations—those of C, $\langle x\rangle$, $\langle x^2\rangle$, the normalization integral for X, and $U(r)$—offer no further difficulties. Finally, it is well known that an ordinary s.c.f. calculation, which is all that remains beyond this stage, is easy for an automatic machine.

The assistance of Mr. James A. Seiler, who did many of the numerical calculations, is gratefully acknowledged.

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[11] For example, a variation calculation for H^- which uses wave functions of the form e^{-br} does not predict binding of the second electron; the use of $(1+ar_{12})\exp[-b(r_1+r_2)]$ immediately yields a very fair approximation to the known electron affinity (reference 6).

[12] It may be worth noting that Thaler (reference 10) found that only the largest term in such an expansion of $\chi(r)$ is of much importance.