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Application of Wave Functions Containing Interelectron Coordinates. II. Approximate Energy Levels of Atoms*

PETER WALSH
Lamp Division, Research Department, Westinghouse Electric Corporation, Bloomfield, New Jersey

AND

SIDNEY BOROWITZ
Physics Department, New York University, New York, New York

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This paper explores further the use of interelectron coordinates in constructing atomic wave functions. A simple method is developed for constructing wave functions of this type which yields surprisingly good values for the energy of a variety of atomic systems, in zero order. The Hamiltonian for the system is split into an unperturbed part, which is separable and which contains the interelectron potentials as well as the electron-nucleus potentials, and into a perturbing term which is always finite and which vanishes whenever an electron is far from the nucleus. The zero-order energies corresponding to this splitting of the Hamiltonian are at least an order of magnitude better for the light atoms than the energies given by the usual Thomas-Fermi theory, and are considerably better than the energies calculated with hydrogenic functions alone in first order.

1. INTRODUCTION

SEVERAL years ago, Pluvinage[1] illustrated, for helium, a method in which interelectron coordinates could be used to separate partially the Schrödinger wave equation so that both the interelectron potentials and the electron-nucleus potentials were taken into the unperturbed part of the Hamiltonian. In the first paper of this series[2] Pluvinage's approach was modified and an approximation technique was developed so that variational values of the energy of systems beyond helium could be accurately calculated. The ground-state energy of lithium was calculated and the result obtained indicated that Pluvinage's approach held excellent promise for other systems.

In this paper, the method of Pluvinage is modified in a different way in order to obtain relatively simple zero-order wave functions which include correlation. The unperturbed Hamiltonian is separable and the resulting differential equations are hydrogenic in character. Thus, the ground-state or the excited-state energy of a variety of atomic systems can be explicitly written down. The results obtained are considerably better than those obtained using hydrogenic functions in zero or in first order, or using the Thomas-Fermi method. The zero-order energies we calculate are surprisingly close to variational energies calculated using the hydrogenic wave functions without explicit r_{ij} dependence.

The motivation behind this paper was to obtain a separation of the Hamiltonian for atomic systems which leads to a solvable unperturbed problem and to a perturbing term which is truly small. In addition, of the many possible solutions to the unperturbed Hamiltonian only those are chosen which display the physical behavior expected of the system.

The actual method adopted was as follows. A full set of dependent interelectron coordinates is introduced in addition to the usual independent coordinates of the electron with respect to the nucleus. We shall refer to these electron coordinates with respect to the nucleus simply as hydrogenic coordinates from now on. The mathematical questions raised by the introduction of additional coordinates, and the relationship of the new problem to the original one will be discussed in an Appendix. With these variables, the Hamiltonian can be split into an unperturbed part and a perturbing part. The unperturbed Hamiltonian is itself separable in the various hydrogenic and interelectron coordinates. It contains all of the potentials present in the system and is exactly solvable. The perturbing Hamiltonian differs from that used previously[1,2] in that it vanishes whenever an electron is far from the nucleus while still remaining finite when any coordinate vanishes. This perturbing term is small compared to the Coulomb interactions in the neighborhood of the Coulomb singularities and is comparable to the Coulomb potentials at large distances from the atom where the Coulomb potentials and the perturbing term are both small. We then hope that the perturbing term, chosen this way, would be small throughout all of space. The zero-order wave function is a product of the individual hydrogenic and interelectron wave functions while the zero-order energy is a sum of the individual hydrogenic and interelectron energies. To specify in detail the zero-order solutions, suitable boundary conditions must be introduced. As usual, the part of the wave function expressed in the hydrogenic coordinates must vanish at infinity and be finite at the nucleus. This leads to the bound-state hydrogenic func-

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[1] P. Pluvinage, Ann. phys. 12, 10 (1950).

[2] P. Walsh and S. Borowitz, Phys. Rev. **115**, 1206 (1959); hereafter referred to as I. The material in this paper on the two electron system had previously been done but not published by M. Kelly and L. Spruch. Reference to their contribution was inadvertently omitted in our first paper. This material has since been published [L. Spruch and M. Kelly, Phys. Rev. **116**, 911 (1959)].

tions for this part. We impose boundary conditions on the interelectron wave functions to account for the physical behavior expected of the system; namely, that when an individual electron is far from the nucleus, the nuclear charge is shielded by the remaining electrons. The part of the wave function containing the interelectron coordinates is required to account for this shielding at large distances from the nucleus. This uniquely determines this part of the wave function and leads immediately to appropriate zero-order energies.

The method we have used does not have exact mathematical validity. It does have, however, a certain physical plausibility which we shall discuss in Appendix 1.

In Sec. 2 of this paper, the general form of the Hamiltonian is presented and discussed when the interelectron coordinates are introduced in addition to the hydrogenic radial and angular coordinates generally used. In Sec. 3, the separation of the Hamiltonian into a perturbed and an unperturbed part is presented. The boundary conditions to be used on the hydrogenic and interelectron parts of the wave function are given in Secs. 4 and 5. The solution of the unperturbed wave equation under the boundary conditions imposed is easily carried out and the zero-order energy is obtained immediately. In Sec. 6, application is made to various charged, neutral and excited atoms to illustrate the method and its results. The results are discussed in Sec. 7 and comparison is made there with other methods for calculating atomic energies.

2. HAMILTONIAN WITH INTERELECTRON COORDINATES

The Hamiltonian for the Schrödinger equation is written in atomic units as

$$H=-\frac{1}{2}\sum_i \nabla_i^2-\sum_i \frac{Z}{r_i}+\frac{1}{2}\sum_{i\neq j}\sum \frac{1}{r_{ij}}. \tag{2.1}$$

Z is the nuclear charge and the summations run over the N electrons present within the atom. The interelectron potentials, $1/r_{ij}$, prevent the exact solution of this Schrödinger equation. The fact that these potentials are singular and numerous prevents any great success in treating them as perturbations. This difficulty can be overcome to a large extent by introducing the interelectron coordinates explicitly.

We now introduce the interelectron coordinates into the problem according to the following procedure: In the Hamiltonian for the system, expressed in spherical polar coordinates in 2.1, we replace $\partial/\partial r_i$ and $\partial/\partial\theta_i$ by the formulas given by the usual rules of partial differentiation,[3] namely

$$\frac{\partial}{\partial r_i}=\frac{\partial}{\partial r_i}+\left(\frac{\partial}{\partial r_{ij}}\right)\frac{\partial r_{ij}}{\partial r_i}, \tag{2.2}$$

where

$$r_{ij}^2=r_i^2+r_j^2-2r_ir_j[\cos\theta_i\cos\theta_j+\sin\theta_i\sin\theta_j\cos(\phi_i-\phi_j)]$$
$$=(x_j-x_i)^2+(y_j-y_i)^2+(z_j-z_i)^2.$$

A relationship similar to (2.2) holds for the partial derivatives with respect to θ_i. The result is

$$\begin{aligned}H=\sum_i\bigg\{-\frac{1}{2}\bigg[\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial}{\partial r_i}\right)+\frac{1}{r_i^2\sin\theta_i}\frac{\partial}{\partial\theta_i}\left(\sin\theta_i\frac{\partial}{\partial\theta_i}\right)\\
+\frac{1}{r_i^2\sin^2\theta_i}\frac{\partial^2}{\partial\phi_i^2}\bigg]-\frac{Z}{r_i}\bigg\}+\frac{1}{2}\sum_{i\neq j}\sum\bigg[-\frac{1}{r_{ij}^2}\frac{\partial}{\partial r_{ij}}\\
\times\left(r_{ij}^2\frac{\partial}{\partial r_{ij}}\right)+\frac{1}{r_{ij}}\bigg]+\sum_{i\neq j}\sum\frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_ir_{ij}}\frac{\partial^2}{\partial r_i\partial r_{ij}}\\
-\sum_{i\neq j}\sum\frac{\boldsymbol{\theta}_i\cdot\mathbf{r}_{ij}}{r_ir_{ij}}\frac{\partial^2}{\partial\theta_i\partial r_{ij}}-\sum_{i\neq j}\sum\frac{\boldsymbol{\phi}_i\cdot\mathbf{r}_{ij}}{r_i\sin\theta_ir_{ij}}\frac{\partial^2}{\partial\phi_i\partial r_{ij}}\\
-\frac{1}{2}\sum_{i\neq j\neq l}\sum\sum\frac{\mathbf{r}_{ij}\cdot\mathbf{r}_{il}}{r_{ij}r_{il}}\frac{\partial^2}{\partial r_{ij}\partial r_{il}},\end{aligned} \tag{2.3}$$

where $\boldsymbol{\theta}_i$ and $\boldsymbol{\phi}_i$ are unit vectors given by

$$\begin{aligned}\boldsymbol{\theta}_i&=\cos\theta_i\cos\phi_i\mathbf{i}+\cos\theta_i\sin\phi_i\mathbf{j}-\sin\theta_i\mathbf{k},\\ \boldsymbol{\phi}_i&=-\sin\phi_i\mathbf{i}+\cos\phi_i\mathbf{j}.\end{aligned} \tag{2.4}$$

The partial derivatives operate on the corresponding coordinates only where they appear explicitly in the wave function.

In principle we now seek a solution of the eigenvalue problem of the differential equation involving the augmented Hamiltonian. Actually we will find only an approximate solution. Since we do not know what boundary conditions to place on the r_{ij} variables considered as independent coordinates which will lead us back to a solution of the original problem, the introduction of the redundant coordinates causes some difficulty. The procedure we adopt is to construct an approximate solution of the more elaborate equation which satisfies some reasonable boundary conditions for the original problem when the constraint $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$ is imposed. This seems like a good physical procedure even if a questionable mathematical one. The point is discussed further in Appendix 1.

Note that the introduction of the dependent r_{ij} does not destroy the orthogonality among the r_i, θ_i, and ϕ_i and, consequently, there are no terms coupling these variables directly. The lack of orthogonality between these variables and the r_{ij}, and among the r_{ij}, account for the coupling terms which are present.

Extending Pluvinage's idea, we can see from (2.3) how the total potential energy could be included in zero order. The first two summations on the right might be taken to represent the unperturbed Hamiltonian (we shall not do this exactly). The corresponding zero-order Schrödinger equation is then separable in the r_i, θ_i, ϕ_i,

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[3] P. Franklin, *Methods of Advanced Calculus* (McGraw-Hill Book Company, New York, 1944), 1st ed., Chap. 2.

and r_{ij} coordinates. The zero-order solution is a product of the individual solutions for each of the coordinates, hydrogenic and interelectronic, while the zero-order energy is a sum of the zero-order energies obtained for each coordinate when the proper boundary conditions are imposed. The fact that the r_{ij} are dependent variables would make it difficult to carry out integrations involving this solution over all space to determine, say, the normalizing constant. The element of volume is $\prod_i r_i^2 \sin\theta_i dr_i d\theta_i d\phi_i$. The r_{ij} in the zero-order wave function must first be expressed in terms of the radial and angular variables as above and then the integrations performed. For any complicated system, such integrations must invariably be done approximately and one particular method of doing so accurately was described in I. This emphasizes the importance of obtaining the best zero-order solution possible in the hope that accurate information can be obtained by examining just the zero-order case.

3. SEPARATION OF THE HAMILTONIAN

A possible method of separating the Hamiltonian, once the interelectron coordinates are introduced, was suggested in the previous section. For reasons given below, the actual separation chosen is somewhat different. Instead, we set $H=H_0+H'$ where

$$H_0=\sum_i\left\{-\frac{1}{2}\left[\frac{1}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial}{\partial r_i}\right)+\frac{1}{r_i^2\sin\theta_i}\frac{\partial}{\partial\theta_i}\times\left(\sin\theta_i\frac{\partial}{\partial\theta_i}\right)+\frac{1}{r_i^2\sin^2\theta_i}\frac{\partial^2}{\partial\phi_i^2}\right]-\frac{Z}{r_i}\right\}+\frac{1}{2}\sum\sum_{i\neq j}\left\{-(1+b_{ij})\frac{\partial^2}{\partial r_{ij}^2}-\frac{2}{r_{ij}}\frac{\partial}{\partial r_{ij}}+\frac{1}{r_{ij}}\right\}, \tag{3.1}$$

$$H'=-\sum\sum_{i\neq j}\left(-\frac{1}{2}b_{ij}\frac{\partial^2}{\partial r_{ij}^2}-\frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_ir_{ij}}\frac{\partial^2}{\partial r_i\partial r_{ij}}+\frac{\boldsymbol{\theta}_i\cdot\mathbf{r}_{ij}}{r_ir_{ij}}\frac{\partial^2}{\partial\theta_i\partial r_{ij}}+\frac{\boldsymbol{\phi}_i\cdot\mathbf{r}_{ij}}{r_i\sin\theta_ir_{ij}}\frac{\partial^2}{\partial\phi_i\partial r_{ij}}+\frac{1}{2}\sum_{l\neq j,i}\frac{\mathbf{r}_{ij}\cdot\mathbf{r}_{il}}{r_{ij}r_{il}}\frac{\partial^2}{\partial r_{ij}\partial r_{il}}\right). \tag{3.2}$$

The choice given above differs from that suggested in the previous section by the addition of second derivative terms, $-\frac{1}{2}b_{ij}\partial^2/\partial r_{ij}^2$ in the unperturbed Hamiltonian and their subsequent subtraction in the perturbing part. We use the freedom which we have gained by introducing the arbitrary constants b_{ij} to make the perturbation vanish in the asymptotic regions of space.

The zero-order wave function is then

$$\Psi_0=\prod_i[\Phi_i(r_i,\theta_i,\phi_i)\prod_{j>i}u_{ij}(r_{ij})]. \tag{3.3}$$

The Φ_i are the hydrogenic wave functions[4] for an atom of charge Z

$$\Phi_i(r_i,\theta_i,\phi_i)=R_{n_il_i}(r_i)Y_{l_im_i}(\theta_i,\phi_i), \tag{3.4}$$

where R represents the radial eigenfunctions while Y represents the angular spherical harmonics. n, l, and m represent the appropriate orbital quantum numbers.

The u_{ij} satisfy the following equation

$$-(1+b_{ij})\frac{d^2u_{ij}}{dr_{ij}^2}-\frac{2}{r_{ij}}\frac{du_{ij}}{dr_{ij}}+\frac{u_{ij}}{r_{ij}}=E_{ij}u_{ij}. \tag{3.5}$$

The solution of this equation depends on what we choose for the asymptotic behavior of the u_{ij}. We shall insist that Ψ_0 be square integrable. In Sec. 5, we shall see that in order to account for the shielding of the ith electron, we require an exponentially increasing solution of (3.5), i.e., $u_{ij}\sim\exp(q_{ij}r_{ij})$, and that the shielding requirement enables us to determine the q_{ij}. The solution of (3.5) is not an eigenvalue problem. However, in terms of the still undetermined b_{ij} and q_{ij}, the energy is given by (see Appendix 2)

$$E_{ij}=-(1+b_{ij})q_{ij}^2. \tag{3.6}$$

This can be seen directly from the asymptotic behavior of Eq. (3.5).

The scheme for determining the b_{ij} will be discussed in Sec. 4. Thus we shall be able to determine the unperturbed energy knowing nothing but the asymptotic form of the u_{ij}.

The proper antisymmetrization of the zero-order wave function in Eq. (3.3) is a simple generalization of well-known procedures.[5] As expected, the antisymmetrization requires that no two electrons have all four quantum numbers (spin included) the same. At most two electrons, each of opposite spin, can occupy the same atomic orbit. The only way in which we will make use of the antisymmetrization is by applying the Pauli principle in filling these atomic orbits. Otherwise, the zero-order wave function will be used in its unsymmetrized form. One result of this is that the unperturbed Hamiltonian will not be symmetrical in all of the electrons

4. DETERMINATION OF THE b_{ij}

The total unperturbed energy of the system depends on the choice of two arbitrary parameters, b_{ij} and q_{ij}. The latter are fixed, as has been indicated, by the asymptotic behavior of the wave function. The former constants are at our disposal and we choose them to minimize the effects of H'. The potential energy terms in

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[4] H. A. Bethe and E. E. Salpeter, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. XXXV, p. 90 ff.

[5] D. R. Hartree, *The Calculation of Atomic Structure* (John Wiley & Sons, New York, 1957), Chap. 3.

our Hamiltonian

$$V=-\sum_i Z/r_i+(1/2)\sum_{j\neq k}\sum 1/r_{jk} \tag{4.1}$$

are singular at the zeros of r_i and r_{ij}. Since the potential energy is comparable to the kinetic energy, V cannot be thought of as a small perturbation. The introduction of the interelectron coordinates allows all of V to be taken into the unperturbed Hamiltonian, H_0. We can hope to obtain accurate zero-order results if the perturbing Hamiltonian is now small compared to V. At the zeros of r_i, r_{jk}, we note from Eqs. (3.2) and (3.3) that $H'\Psi_0$ is always finite. (This is obvious for the zero angular momentum cases, where the angular derivatives are zero. For other angular momenta the behavior of the $R(r_i)$ cancels the r_i^{-1} in the angular derivative terms near the zeros.) As already mentioned, $V\Psi_0$ becomes infinite at the points in question and the effects of the perturbing Hamiltonian are thus small compared to the zero-order potentials in the regions of space near the nucleus and near each electron, independent of the choice of any arbitrary constants.

The problem is more complex, however, in what we will refer to as the asymptotic region of space, where an electron is far from the nucleus and its companion electrons. In this region we will, of course, want to compare H' with V. Then, by adjusting the b_{ij}, we will make H' vanish in a suitable manner. The first thing to be done is to decide what region of space shall comprise the asymptotic region. After this, we will be able to detail the suitable manner in which H' must vanish.

In order to determine the asymptotic region of space for each electron we picture the atom as being constructed by bringing the electrons in from infinity, filling the atomic shells (determined by the principal quantum number, n) consecutively, starting from the innermost. In our approximation, an electron in an inner shell is not affected by any outer shell, but it is by the electrons in lower shells or in the same shell. Such a picture is simple to apply and allows a unique determination of the shielding requirement imposed as a boundary condition upon the interelectron wave functions in the next section.

Consider an electron, the ith, which occupies the n_i shell. The atom is built up to and including this shell. The asymptotic region for this electron is created by moving the electron outward from the vicinity of the incomplete atom. The Coulomb potential acting upon the electron becomes

$$V_i=-\frac{Z}{r_i}+\sum_{j\neq i}^{P_i}\frac{1}{r_{ij}}\sim\frac{-Z+P_i-1}{r_i}, \tag{4.2}$$

where P_i is the total number of electrons in all shells up to and including the n_i. In the perturbing Hamiltonian, the portion containing the coordinate of the ith particle is

$$\begin{aligned}H_i'=\sum_{j\neq i}^{P_i}\biggl(&-b_{ij}\frac{\partial^2}{\partial r_{ij}^2}-\frac{\mathbf{r}_i\cdot\mathbf{r}_{ij}}{r_ir_{ij}}\frac{\partial^2}{\partial r_i\partial r_{ij}}\\&+\frac{\boldsymbol{\theta}_i\cdot\mathbf{r}_{ij}}{r_ir_{ij}}\frac{\partial^2}{\partial\theta_i\partial r_{ij}}+\frac{\boldsymbol{\phi}_i\cdot\mathbf{r}_{ij}}{r_i\sin\theta_ir_{ij}}\frac{\partial^2}{\partial\phi_i\partial r_{ij}}\\&+\frac{1}{2}\sum_{l\neq j,i}^{P_i}\frac{\mathbf{r}_{ij}\cdot\mathbf{r}_{il}}{r_{ij}r_{il}}\frac{\partial^2}{\partial r_{ij}\partial r_{il}}\biggr).\end{aligned} \tag{4.3}$$

In the asymptotic region the opposing vectors $\mathbf{r}_i$ and $\mathbf{r}_{ij}$ line up. The distance derivatives have the effect of multiplying Ψ_0 by the constants appearing in the exponents of R and u, while the angular derivative terms become negligible because of the extra factor of r_i in the denominator. Then the operator H_i' has the following approximate numerical value:

$$H_i'\sim\sum_{j\neq i}{}'\biggl(-b_{ij}q_{ij}^2-q_{ij}\frac{Z}{n_i}+\frac{1}{2}\sum_{l\neq j,i}{}'q_{ij}q_{il}\biggr)+O\biggl(\frac{1}{r_i}\biggr), \tag{4.4}$$

where we have again assumed that $u_{ij}\sim\exp(q_{ij}r_{ij})$ in the asymptotic region. The sum is over all shells up to and including the n_i shell. This is indicated by the prime on the summation sign.

The perturbation caused by the ith electron thus behaves like a constant in the asymptotic region, while the corresponding Coulomb potential found in the unperturbed term vanishes like $1/r_i$. The b_{ij} we introduced are now adjusted so that H_i' itself will vanish at least as strongly as V_i in the asymptotic region. Therefore we take

$$\sum_{j\neq i}{}'\biggl(-b_{ij}q_{ij}^2-q_{ij}\frac{Z}{n_i}+\frac{1}{2}\sum_{l\neq j,i}{}'q_{ij}q_{il}\biggr)=0. \tag{4.5}$$

This is the prescription we use to insure that the perturbation term is small in the asymptotic region. It is, of course, applied to all the various shells comprising the atom. Note that only n_i enters into the formula, so that all electrons in the same shell, but with different m, l values, are treated identically. The q's are determined by the shielding discussed in the next section.

We now have completed the description of the separation of the Hamiltonian and the determination of the b_{ij}. The perturbation introduced is small compared to the Coulomb potentials near the origins of all the coordinates. In the asymptotic region about each electron, the effect of the perturbation, although comparable to the Coulomb potential, decreases as $1/r$. It is then reasonable to expect that the effect of the perturbation will be small throughout all of the physical space of each electron, and that the zero-order wave function, Eq. (3.3), should accurately represent the system.

The asymptotic behavior of H_i' for the interelectron wave function used in I is worthy of note. The q's were all taken as zero in that paper and all the interelectron wave functions became the same Bessel-Clifford function. The corresponding H_i' thus vanish asymptotically. However, investigation of the Bessel-Clifford function shows that

$$H_i'\Psi_{\mathrm{BC}} \sim O(r_i^{-\frac{1}{2}})\Psi_{\mathrm{BC}}.$$

In addition, the shielding condition we impose in the next section cannot be met by this wave function. Nevertheless, the approach used in I resembles in part the present method and the success found with the Bessel-Clifford function partially validates the method used here.

5. SHIELDING REQUIREMENT

The zero-order wave function has been given in Eq. (3.3). In order to determine the wave functions Φ and u_{ij} completely, suitable boundary conditions must be imposed. Actually in writing Φ as given in Eq. (3.4) we have implicitly assumed one set of boundary conditions. This is that the hydrogenic wave functions are finite at the origin and vanish at infinity. In fact, they must vanish so strongly at infinity that the total wave function Ψ_0 is quadratically integrable. Despite the exponentially increasing behavior which we will demand of the u_{ij} the solution for Ψ_0 satisfies this boundary condition.

What boundary condition shall we impose upon the u_{ij}? The choice, we have indicated earlier, must express the shielding of the nuclear charge which occurs as one electron is moved away from the nucleus.

Let us examine the solution of the Schrödinger equation when the ith electron in the n_i shell is in its asymptotic region as described in the previous section. Mathematically we do this by requiring that r_h/r_i be very small, where the subscript h designates any electron in the same shell or in an inner shell compared to i, while requiring that r_k/r_i be very large where the subscript k represents any electron in the outer shells. The cloud of electrons located in shells outside of the n_i shell will not affect the potential of the ith electron, assuming that these electrons are uniformly distributed. We specifically assume that such is the case, although there are errors involved in this assumption due to the overlap of the wave functions corresponding to different shells. The inner electrons, h, however, will shield the nuclear charge, changing its effective value to $Z-P_i+1$.

That part of the Schrödinger equation corresponding to the ith electron now separates out. If we impose the usual boundary conditions on the solution of this part of the Schrödinger equation, that it be finite at small r_i and vanish at infinity, the corresponding wave function is a hydrogenic wave function bound in some orbit to a charge, $Z-P_i+1$. Under the conditions that r_h/r_i must be small while r_k/r_i is large, the ith electron does not have any possibility of interacting with the other electrons, and it must remain in its original orbit in the n_i shell. Therefore, in the asymptotic region of the ith electron, the zero-order wave function must have a separable part which represents the ith electron as moving in its original shell in the field of a nuclear charge $Z-P_i+1$. This requirement cannot be met in every detail. However, it is easily satisfied as far as the exponential behavior of Ψ_0 is concerned by imposing the following boundary condition on u_{ij} at large distances:

$$\Phi_i(r_i)\prod_{j\neq i}^{P_i} u_{ij}(r_{ij}) \sim \exp\left[\frac{-(Z-P_i+1)r_i}{n_i}\right]. \qquad (5.1)$$

Thus

$$\sum_{j\neq i}^{P_i} q_{ij} = \frac{P_i-1}{n_i}$$

since $\Phi_i(r_i) \sim \exp(-Zr_i/n_i)$ as $r_i \to \infty$.

In view of the equivalent shielding by all the inner electrons, we take all of the q_{ij} as equal. That is

$$q_{ij} = 1/n_i, \quad n_j \leq n_i. \qquad (5.2)$$

Since the outer electrons do not shield the ith, we need not impose any requirement on the q_{ij}, $n_j > n_i$. The argument given above is, of course, not a proof. However, it does establish the reasonableness of our approach. The reason, for instance, why we do not define the asymptotic region for the ith electron by moving this electron out past all of the other electrons becomes obvious from our argument. In passing the ith electron through the cloud of outer electrons, the validity of the original orbital assignment will be destroyed because of the electronic interactions. We cannot say what precise orbit the ith electron will now occupy around the shielded nucleus of charge $Z-N+1$. Again, the similar exponential behavior of different orbital wave functions representing the same shell explains why the treatment is identical for electrons in different orbits within the same shell. Note that only the principal quantum number appears in our equations.

Once we have determined the value of the q's, the equation in the last section which expresses the condition that H_i' vanish asymptotically can be solved. Following the above arguments all the b_{ij} are taken as equal when n_i is less than or equal to n_j. Then Eq. (4.5) yields

$$-(1+b_{ij}) = (2Z-P_i)/2, \quad n_j \leq n_i. \qquad (5.3)$$

By starting with the innermost shell and progressively filling the outer shells, a set of numbers q_{ij} and b_{ij} are easily generated. These q's and b's complete the description of H_0 and Ψ_0. Useful properties of the system can now be obtained by investigating H_0 or Ψ_0 directly. The zero-order energy, for example, is just the sum of all the individual hydrogenic and interelectron energies. From Eq. (3.6) and the properties of the Φ's we have

$$E_0 = -\frac{1}{2}\sum_i \frac{Z^2}{n_i^2} - \sum_{i>j}\sum (1+b_{ij})q_{ij}^2. \qquad (5.4)$$

Various applications of this equation will now be discussed.

6. APPLICATIONS

Two-Electron Atoms

Helium and helium-like ions consist of two electrons both in the lowest orbit surrounding a nucleus of charge Z. These are the simplest many-electron systems which are encountered. Only the ground-state energy is considered now.

The zero-order wave function is a product of two ground-state hydrogenic wave functions times the interelectron wave function. That is

$$\Psi_0 = e^{-Zr_1}e^{-Zr_2}u(r_{12}). \tag{6.1}$$

When one electron is far from the nucleus it moves in the ground state of a nucleus of shielded charge $Z-1$. Its radial coordinate, say, r_2 becomes very close to the value of r_{12}. The exponential form of u at large values will be $\exp(qr_{12})$ and in order that Ψ_0 display the proper shielding at larger r we demand

$$e^{-Zr_1}e^{-Zr_2}e^{qr_{12}} \sim e^{-Zr_1}e^{-(Z-1)r_2}. \tag{6.2}$$

Thus

$$q=1, \tag{6.3}$$

in agreement with Eq. (5.2).

The perturbing Hamiltonian H_2' for the second electron is given by Eq. (4.3)

$$H_2'\Psi_0 = \left(b\frac{\partial^2}{\partial r_{12}^2} - \frac{\mathbf{r}_2\cdot\mathbf{r}_{12}}{r_2 r_{12}}\frac{\partial^2}{\partial r_2 \partial r_{12}} \right)\Psi_0. \tag{6.4}$$

At large r_2 the vectors $\mathbf{r}_2$ and $\mathbf{r}_{12}$ line up and H_2' approaches the numerical value

$$H_2' = bq^2 + Zq. \tag{6.5}$$

In order to have H_2' vanish asymptotically, we require

$$b=-Z. \tag{6.6}$$

This agrees with Eq. (5.3).

The total ground-state energy in zero order is the sum of the separate nuclear and interelectron energies. Thus, using Eq. (3.6),

$$E_0 = -Z^2 - (1+b)q^2 = -Z^2 + Z - 1, \tag{6.7}$$

in view of Eqs. (6.3) and (6.6). The corresponding zero-order energy using only the hydrogenic functions is just

$$E_0^{\mathrm{H}} = -Z^2. \tag{6.8}$$

Table I presents the zero-order energies calculated using interelectron functions, and also using only hydrogenic functions. These results are given in terms of the percent deviation, Δ, from the true value:

$$\Delta = 100(E_{\mathrm{expt}} - E_{\mathrm{calc}})/E_{\mathrm{expt}}. \tag{6.9}$$

Table I. Comparison of percentage deviations, Δ_0^{H}, Δ_0, of calculated zero-order energies (in atomic units) from the experimental energies using hydrogenic functions and using the method of this paper.

System	E_{exp}(a.u.)	Δ_0^{H}	Δ_0
Helium-like			
He	−2.904	−37.9	−3.3
Li$^+$	−7.29	−23.5	+4.0
Be^{2+}	−13.67	−17.0	+4.9
B^{3+}	−22.04	−13.4	+4.7
C^{4+}	−32.4	−11.1	+4.3
N^{5+}	−44.8	−9.4	+4.0
O^{6+}	−59.2	−8.1	+3.7
F^{7+}	−75.5	−7.2	+3.4
Excited helium[a]			
$2\,^{1,3}S_0$	−2.162	−15.6	−4.1
$3\,^{1,3}S_0$	−2.065	−7.5	−2.2
$4\,^{1,3}S_0$	−2.038	−4.3	−1.2

[a] The experimental values for excited helium are an average of the singlet and triplet values.

Excited States of Helium

An excited two-electron atom is the simplest atomic system involving more than one orbit. Consider one electron in the inner lth shell and the other electron in the outer mth shell. The inner electron shields the outer electron from the nuclear charge but sees the full nuclear charge itself. The zero-order wave function is

$$\Psi_0 = \Phi_l(r_1)\Phi_m(r_2)u_{lm}(r_{12}). \tag{6.10}$$

At large distances this has the asymptotic behavior, $\exp(-Zr_1l^{-1} - Zr_2m^{-1} + qr_{12})$. When the outer electron is far from the nucleus, the shielding produced by the inner electron requires the behavior, $\exp[-Zr_1l^{-1} - (Z-1)r_2m^{-1}]$. Therefore, $q=1/m$. There is no equation to express shielding of the inner electron because there are no electrons in still lower orbits than it. The perturbation H_2' has the asymptotic value [see Eqs. (4.3) and (6.5)]

$$H_2' = (b+Z)/m^2. \tag{6.11}$$

As in the unexcited case, we must choose $b=-Z$.

The total zero-order energy now becomes

$$E_0 = -\frac{1}{2}\left(\frac{Z^2}{l^2} + \frac{Z^2}{m^2}\right) + \frac{(Z-1)}{m^2}. \tag{6.12}$$

The corresponding zero-order hydrogenic energy is

$$E_0^{\mathrm{H}} = -\frac{1}{2}\left(\frac{Z^2}{l^2} + \frac{Z^2}{m^2}\right). \tag{6.13}$$

The deviation of these energies from the experimental values are presented in Table I for the singly excited states of helium.

Ground State of Neutral Atoms

We now treat the ground state of neutral atoms within the periodic chart. The atoms are treated by starting with the innermost shell and filling the shells successively. Those orbits with the same principal quantum number are considered equivalent. Once an inner shell is filled no further change occurs in the manner of treating that shell.

The first shell is filled with helium. The contribution E_{01} to the zero-order energy from this completed shell as we progress along the periodic chart changes only because of the variation in Z. This contribution has already been given by Eq. (6.7) as $-Z^2+Z-1$.

Consider the electrons in the second principal orbit $n=2$. As one of these electrons is moved to infinity, the electrons remaining in the second and first orbit shield the nucleus. Since the q_{2j} are all identical, Eq. (5.2) yields $q_{2j}=\frac{1}{2}$, $n_j\leq 2$.

The perturbation terms linking this shell to lower shells must vanish asymptotically. The requirement is fulfilled by Eq. (5.3). There are $[P_2(P_2-1)-2]/2$ interelectron coordinates linking the second shell to itself or lower shells. Therefore, the zero-order contribution to the energy from the second shell is

$$E_{02}=\frac{-Z^2}{2}\left(\frac{P_2-2}{4}\right)+\frac{1}{4}\left(Z-\frac{P_2}{2}\right)\left(\frac{P_2(P_2-1)}{2}-1\right). \tag{6.14}$$

When this shell is filled $P_2=10$ and E_{02} has the value $-Z^2+11Z-55$. In a similar manner, contributions from the outer shells can be calculated rapidly. For instance, the third shell contributes the energy

$$E_{03}=\frac{-Z^2}{2}\left(\frac{P_3-10}{9}\right)+\frac{1}{9}\left(Z-\frac{P_3}{2}\right)\left(\frac{P_3(P_3-1)}{2}-45\right), \tag{6.15}$$

while the rth shell has the energy

$$E_{0r}=\frac{-Z^2}{2}\left(\frac{P_r-P_{r-1}}{r^2}\right)+\frac{1}{r^2}\left(Z-\frac{P_r}{2}\right)\times\left(\frac{P_r(P_r-1)}{2}-\frac{P_{r-1}(P_{r-1}-1)}{2}\right). \tag{6.16}$$

The total zero-order energy is the sum of the various energies of the filled or partially filled shells. The corresponding zero-order contribution using only hydrogenic functions is, of course

$$E_{0r}{}^{\mathrm{H}}=-Z^2(P_r-P_{r-1})/2r^2. \tag{6.17}$$

The energies calculated with the above formulas are given in Table II, in terms of their deviation from the experimental values.

7. DISCUSSION

Table I presents the comparative energy deviations calculated in zero-order with the use of hydrogenic functions and with the method as outlined in this paper for various excited and ionized two-electron atoms. As noted in Appendix I, our method is not applicable to the case, $Z=1$. The introduction of interelectron coordinates together with the proper shielding requirements produces a very substantial gain in accuracy. This is illustrated more forcibly in Table II where results for various neutral atoms are given. It is apparent that hydrogenic functions do not yield satisfactory energies for neutral atoms in zero order.

In order to yield improved answers with hydrogenic functions, recourse must be made to first order, or still better, to variational calculations with a consequent large increase in computational effort at each stage. We also present in Table II, these first-order and variational calculations for the hydrogenic functions. The variational results are available and were obtained with the antisymmetrized Morse functions.[6,7] These Morse functions are just the hydrogenic wave functions in which the constants, such as the nuclear charge, are treated as variable parameters. The Morse function calculations are representative of the many different variational calculations in the literature and, furthermore, have been extended over most of the range for which energy values are available. The first-order energies given in the table were obtained by using the formulas given in reference 6 and by taking the wave function as a product of unsymmetrized hydrogenic functions.

Table II shows that the zero-order energies obtained with the introduction of shielded interelectron functions are considerably better than the first-order hydrogenic energies. This is so despite the fact that the zero-order

TABLE II. Percentage deviations for neutral atoms: $\Delta_0{}^{\mathrm{H}}$, $\Delta_1{}^{\mathrm{H}}$, $\Delta_v{}^{\mathrm{H}}$ are the zero-order, first-order, and variational results using hydrogenic functions; Δ^{TF} and Δ_0 are the Thomas-Fermi results and the zero-order results of this paper.

System	E_{exp}(a.u.)[a]	$\Delta_0{}^{\mathrm{H}}$	$\Delta_1{}^{\mathrm{H}}$	$\Delta_v{}^{\mathrm{H}}$	Δ^{TF}	Δ_0
He $^1S_0$	−2.904	−37.9	+5.3	+1.9(1)[b]	−33.5	−3.3
Li $^2S_{0\frac{1}{2}}$	−7.49	−35.2	+6.7	+0.9(3)	−33.3	+1.5
Be $^1S_0$	−14.68	−36.2	+7.8	+0.8(4)	−33.0	+1.2
B $^2P_{0\frac{1}{2}}$	−24.67	−39.3	+9.8	+0.6(4)	−33.3	−0.3
C $^3P_0$	−37.9	−42.6	+11.5	+0.6(4)	−32.7	−1.6
N $^4S_{1\frac{1}{2}}$	−54.6	−45.7	+12.9	+0.6(4)	−32.0	−2.7
O $^3P_2$	−75.2	−49.0	+14.2	+0.8(4)	−30.9	−3.7
F $^2P_{1\frac{1}{2}}$	−99.9	−52.0	+15.2	+1.0(4)	−29.7	−4.6
Mg $^1S_0$	−200.3	−52.1	···	···	−26.6	−0.3
Al $^2P_{0\frac{1}{2}}$	−242.7	−51.0	···	···	−25.9	+0.2

[a] Experimental values (in atomic units) are from *Atomic Energy Levels*, edited by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1952), Vol. II as extended somewhat by R. Cowan and J. Ashkin, reference 10.

[b] The numbers in parenthesis are the number of variable parameters used.

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[6] P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. **48**, 948 (1935).

[7] A. Tubis, Phys. Rev. **102**, 1049 (1956).

results are enormously more simple to obtain, involving only algebra and no integration. Indeed, our zero-order energies are surprisingly close to the variational energies.

Another widespread and relatively simple method for obtaining the energies of neutral atoms is the Thomas-Fermi calculation. This calculation is based on a variational approach[8]; however, because of the mathematical approximations introduced within the theory,[9] accuracy in the energy values comparable to usual variational calculations cannot be expected. Table II presents the deviations calculated by the usual Thomas-Fermi expression, $E_{\mathrm{TF}}=0.769Z^{7/3}$. These results compare very poorly with our zero-order calculations for the light atoms given in Table II, the Thomas-Fermi energy deviations being an order of magnitude larger than the zero-order deviations. The experimental energies for the light atoms have been extended analytically to heavier atoms by Mayer and these energies have been reported by Cowan and Ashkin.[10] Figure 1 compares the Thomas-Fermi energies and our zero-order energies with the experimental values over the extended range of Z up to those values of Z where relativistic corrections become important. No significant improvement of the Thomas-Fermi results over the zero-order calculations is found within this range.

Some words should be said here about the applicability of the type of shielding we introduced as a boundary condition upon the interelectron wave functions. This discussion may help us to understand how the results we obtained can be adapted to other types of quantum-mechanical systems. It should be remembered that the outer shells were neglected in treating the asymptotic shielding of any orbit, while all subshells in the same shell were treated identically. Such a procedure will be expected to work well whenever the atomic system possesses well separated shells together with an approximately central field. The characteristic of the Coulomb potential is that it does, indeed, produce well separated shells and the central field approximation is certainly excellent for all the filled shells within the atom. Thus our approach should describe very well the behavior of the inner shells in an atom and these shells, of course, contribute the major part to the total energy of the atom. The presence of p, d, $\cdots$ shells outside of filled shells should disturb the results somewhat, but such inaccuracies will disappear once the shell is filled. A glance at Table II confirms these expectations in a general way. Note the extremely good results once a shell is completed in comparison to the progressive worsening while the shell is being filled.

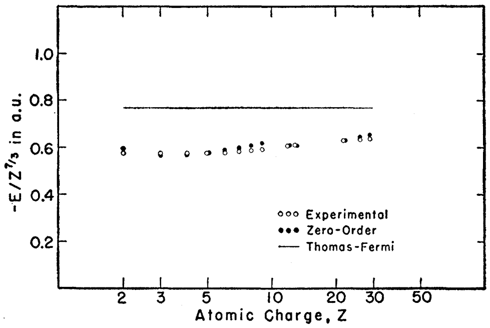

FIG. 1. Comparison of the Thomas-Fermi energies and the zero-order energies of this paper with the experimental energies of neutral atoms (in atomic units). The experimental values for Z up to 13 are as given in Table II while the last three experimental values are actually analytical values due to Mayer as reported in reference 10.

A final note will be made concerning the applications of first-order perturbation theory with our zero-order wave functions, Ψ_0. Because of the interelectron functions, the wave functions, Ψ_{0p}, generated by allowing the individual electrons to fill all of the possible orbits are not completely orthogonal among themselves. This is so because H' is not zero. If it were, we would have $H_0=H$ and the set, Ψ_{0p}, would be orthogonal simply because of the Hermitian properties of H. However, our method of approach has been aimed at making H' small compared to H_0 and the results obtained certainly indicate that this aim has been accomplished. We can then be fairly confident that the set of functions, Ψ_{0p}, is quasi-orthogonal in the sense that (Ψ_{0p},Ψ_{0q}) is much smaller than either (Ψ_{0p},Ψ_{0p}) or (Ψ_{0q},Ψ_{0q}). This, plus the fact that $H_0\simeq H$ will allow us to take over the usual first-order perturbation formulas directly for use with the set Ψ_{0p} with the expectation that any inaccuracies will affect the results in second-order only.

APPENDIX 1

We shall illustrate the basic procedure we have used in this paper by introducing redundant coordinates in a one dimensional problem. Using this as a model it will become clearer what the mathematical content of the more complicated problem treated in the body of the paper is.

Suppose the Hamiltonian of our system is $H(x)=-\frac{1}{2}d^2/dx^2+V(x)$ and the original equation is

$$H(x)\phi(x)=E\phi(x). \qquad \mathrm{A}(1.1)$$

By imposing suitable boundary conditions, we can specify the solution of A(1.1) corresponding to a particular energy. Figure 2 shows a curve which might be a portion of such an eigenfunction. We next parametrize a portion of $\phi(x)$, by substituting $y=y(x)$ in it, so that

$$\phi(x)=\psi(x,y(x)).$$

This procedure is not unique, but its lack of uniqueness is unimportant for our considerations. We now can plot the function $\psi(x,y(x))$ in the x, y, ψ space and the effect

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[8] P. Gombas, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XXXVI, p. 120 ff.

[9] N. H. March and J. S. Plaskett, Proc. Roy. Soc. (London) **A235**, 419 (1956).

[10] R. D. Cowan and J. Ashkin, Phys. Rev. **105**, 144 (1957).

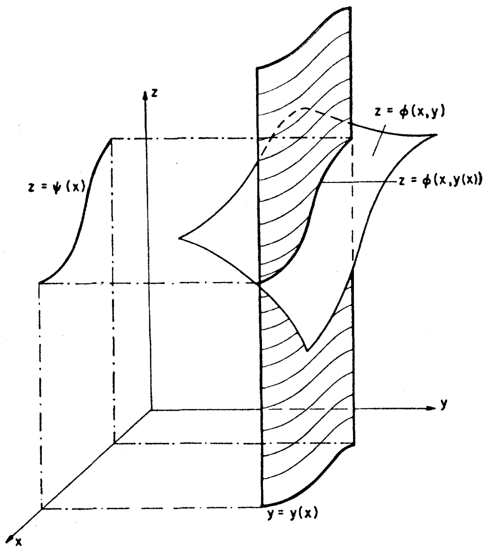

FIG. 2. Relationship of $\psi(x,y)$, $\phi(x)$, and $y=y(x)$.

is to deform the plane curve $\phi(x)$ into some space curve. $\phi(x)$ is the projection of $\psi(x,y(x))$ onto the $x-\phi$ plane.

We now require that the derivatives of the plane curve $\phi(x)$ be equal to the derivatives of the space curve $\psi(x,y(x))$. This means that

$$\frac{d}{dx}\longrightarrow \underset{\Delta x\to 0}{L}\frac{\psi(x+\Delta x,\, y(x+\Delta x))-\psi(x,y(x))}{\Delta x}$$

$$=\frac{\partial\psi}{\partial x}+\frac{\partial\psi}{\partial y}\frac{dy}{dx}, \qquad \mathrm{A}(1.2)$$

which is the chain rule of differentiation we have used. The original Hamiltonian $H(x)$ is thus replaced by a Hamiltonian $H(x,y)$ which is equivalent to it on the curve $\psi(x,y(x))$. This Hamiltonian is not unique, depending as it does on the parametrization $y(x)$ we have used but again its lack of uniqueness is irrelevant.

Let us now consider the larger problem in the three-dimensional space

$$H(x,y)\psi(x,y)=E\psi(x,y), \qquad \mathrm{A}(1.3)$$

If the surfaces $\psi(x,y)$ contain the curve $\psi(x,y(x))$, then $\psi(x,y(x))=\phi(x)$ is an eigenfunction of the original problem corresponding to the energy associated with $\phi(x)$. For the larger problem we have no way of specifying a suitable boundary condition in the y variable to ensure that the surface contain the curve $\psi(x,y(x))$.

The procedure we have followed in the text is to guess at reasonable, approximate solutions of A(1.3) which contain a curve corresponding to an approximate $\psi(x,y(x))$ which in turn satisfy reasonable boundary conditions when projected onto the $x-\phi$ plane. Since our approximate solutions in the larger space have this property when projected, we consider that they are reasonable representations of the eigenfunctions of the problem corresponding to A(1.1).

We might add that we have used this technique for solving approximately the one-dimensional harmonic oscillation with success comparable to that quoted in this paper for atoms.

APPENDIX 2

The solution to the equation of the interelectron wave function,

$$(1+b)\frac{d^2u}{dr^2}+\frac{2}{r}\frac{du}{dr}-\frac{u}{r}+Eu=0, \qquad \mathrm{A}(2.1)$$

has the form

$$u=e^{qr}\,{}_1F_1\left(\frac{2q-1}{2q(1+b)},\frac{2}{1+b},-2qr\right), \qquad \mathrm{A}(2.2)$$

where $q=\pm[-E/(1+b)]^{\frac{1}{2}}$ and ${}_1F_1$ is the confluent hypergeometric function.[11] At large values of r and for real q, $e^{qr}\,{}_1F_1$ has the dependence $\exp(+|q|r)$. This is the exponentially increasing solution in r at infinity which is needed to fulfill the shielding requirement.

For the hydrogen negative ion, $(b+1)$ has the value 0. The solution of Eq. A(2.1) for that case is $n(0)\exp[(Er^2/4)-(r/2)]$. This does not have the exponential behavior we need and our method is not applicable in that particular instance. This result is not surprising since we have neglected the polarization of the atom by the added electron and the binding of H^- depends wholly on this polarization.

It is worth noting that the integrals necessary to obtain the atomic energies from the variational formula $E=(\Psi_0,H\Psi_0)/(\Psi_0,\Psi_0)$ can be carried out in closed form for two electron systems when A(2.2) is used as the interelectron wave function. For these systems the Hylleraas[12] variables are introduced and integrals of the following types are found[1,2]:

$$J_n(Z)=\int e^{-2(Z-1)}\{{}_1F_1[-1/2(Z-1),$$

$$-2/(Z-1),\,-2r]\}^2r^ndr. \qquad \mathrm{A}(2.3)$$

These are evaluated by the formulas given by Alder and Winther.[13] The final result is

$$J_n=\frac{n!}{[2(Z-1)]^{n+1}}F_2\left[n+1,\frac{-1}{2(Z-1)},\frac{-1}{2(Z-1)},\right.$$

$$\left.\times\frac{-2}{Z-1},\frac{-2}{Z-1},\frac{-1}{Z-1},\frac{-1}{Z-1}\right], \qquad \mathrm{A}(2.4)$$

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[11] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, New York, 1953), Vol. I.

[12] E. A. Hylleraas, Z. Physik **54**, 374 (1929).

[13] K. Alder and A. Winther, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **29**, 18 (1955).

where F_2 is the generalized hypergeometric function in two variables.[14]

An approximation technique was given in I for evaluating integrals containing many interelectron functions. For greatest accuracy, the technique depended upon the evaluation of integrals of the type, J_n. Equation A(2.4) thus allows this approximation technique to be used with the wave functions of this paper.

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[14] P. Appell and J. Kampé de Fériet, *Fonctions Hypergéométriques*, etc. (Gauthiers-Villars, Paris, 1926).

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Variational Treatment of Electron-Hydrogen Atom Elastic Scattering

SYDNEY GELTMAN
National Bureau of Standards, Washington, D. C.

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The Hulthén-Kohn variational method is applied to the elastic scattering of electrons by hydrogen atoms. The trial function used is of a nonseparable form, allows for the virtual excitation of the 2*s* and 3*s* states, and contains a scaling parameter which is allowed to vary. The resulting scattering lengths and *S*, *P*, and *D* singlet and triplet phase shifts are compared with the results of other calculations, and reasons are given for expecting them to be of improved accuracy.

I. INTRODUCTION

THE elastic scattering of electrons by hydrogen atoms is the simplest example of atomic scattering involving a composite system. As such it is not tractable by exact analytic means, and has been the subject of numerous successively improved calculations involving various approximation techniques. As there have recently appeared several papers[1] containing excellent reviews of the subject, we will not attempt to include one here. This paper is concerned with a Hulthén-Kohn variational calculation for the *S*, *P*, and *D* phase shifts, making use of a more flexible trial function than has so far been used. It is expected that this will substantially improve the existing values in a manner similar to the rapid improvement of the bound-state energy of a two-electron system when more elaborate trial functions are used in the Ritz variational procedure.

II. HULTHÉN-KOHN VARIATIONAL METHOD

In the atomic units in which length is expressed in Bohr radii and energy in double rydbergs, the Hamiltonian for the electron-hydrogen atom system is

$$H=-\tfrac{1}{2}\nabla_1{}^2-\tfrac{1}{2}\nabla_2{}^2-\frac{1}{r_1}-\frac{1}{r_2}+\frac{1}{r_{12}}. \qquad (1)$$

The asymptotic boundary condition for a given trial partial wave function satisfying the Schrödinger equation,

$$(H-E)\Psi=0, \qquad (2)$$

may be expressed as

$$\Psi_t \underset{r_1\to\infty}{\sim} \psi_0(r_2)Y_{l0}(\hat{\mathbf{r}}_1)r_1{}^{-1} \times\begin{cases} b_t\sin(kr_1-\frac{1}{2}l\pi)+a_t\cos(kr_1-\frac{1}{2}l\pi) \\ \text{or} \\ \mathcal{A}\sin(kr_1+\eta_t-\frac{1}{2}l\pi), \end{cases} \qquad (3)$$

where $\psi_0(r)$ is the ground-state hydrogen wave function $e^{-r}/\sqrt{\pi}$, and $Y_{l0}(\hat{\mathbf{r}}_1)$ is the normalized Legendre polynomial $[(2l+1)/4\pi]^{\frac{1}{2}}P_l(\cos\theta_1)$; $\hat{\mathbf{r}}\equiv\mathbf{r}/r$. In addition to the above asymptotic condition, the trial function must (1) be symmetric or antisymmetric in $\mathbf{r}_1$ and $\mathbf{r}_2$, (2) satisfy the boundary conditions at the origin of $\mathbf{r}_1$ and $\mathbf{r}_2$, and (3) be an eigenfunction of the *z* component and square of the total angular momentum.

Consider the integral

$$L_t=\int\int\Psi_t(H-E)\Psi_t d\tau_1 d\tau_2, \qquad (4)$$

in which Ψ_t satisfies all the preceding conditions and contains the additional variational parameters c_1, c_2, $\cdots c_n$. The Hulthén-Kohn stationary expression is

$$\delta L_t=\mathcal{A}^2 k\delta\eta_t=k[b_t\delta a_t-a_t\delta b_t]. \qquad (5)$$

The variation in L_t is performed with respect to all other parameters that may be contained by Ψ_t as well as the asymptotic parameters, η_t, a_t, and b_t. As we may choose the asymptotic amplitude to be $\mathcal{A}=1$, the two phase parameters a_t and b_t cannot be varied independently. Choosing $a_t=1$ and $\delta a_t=0$ leads to the second Hulthén method[2] (called this to differentiate from the original Hulthén method), with the condition

$$\delta L_t=-k\delta b_t, \qquad (6)$$

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[1] H. S. W. Massey, Revs. Modern Phys. **28**, 199 (1956); B. H. Bransden, A. Dalgarno, T. L. John, and M. J. Seaton, Proc. Phys. Soc. (London) **71**, 877 (1958); F. B. Malik, Z. Naturforsch. **14a**, 172 (1959).

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