and is related to the result by

$$P(k)=(8i/3)S(2). \tag{9}$$

The result is[3]

$$P(k)=\frac{16}{k^2}\left|\frac{1-\lambda}{1+\lambda}\right|^{1/\lambda}\int_1^{1/\lambda}\frac{dt}{(1+t)^4}(1-t^2\lambda^2)\left|\frac{1+\lambda t}{1-\lambda t}\right|^{1/\lambda} \tag{10}$$

where $\lambda=(1-k)^{1/2}$. This has been evaluated numerically with the aid of an IBM 650 in the range $-0.7<k<0.7$. Results are presented below. Figure 1 displays $P(k)$ in this range. Figure 2 gives the ratio of the cross section to the Thomson cross section vs $k$ in units of rydbergs (13.6 eV). We note that $P(k)\rightarrow\frac{1}{2}$ as $k\rightarrow 0$ so that the cross section vanishes (as $k^4$) as the incident photon "sees" less and less atomic structure. In the high-energy limit, $P(k)+P(-k)\sim 1/k^2$ so that the binding becomes unimportant and the scattering takes place as though from a free electron.

$P(k)$ is singular for $k=\frac{3}{4}$, the first threshold. The singularity is, of course, nonphysical. We have omitted the finite linewidth from our description of the intermediate states in (4). Its inclusion would yield a slight shift of the eigenvalues $E_n$, making them complex. $P(k)$ would then exhibit a sharp finite peak at the threshold. If the linewidth were solely due to natural broadening, $P(k)$ would have the value

$$|P(\tfrac{3}{4})|\rightarrow\tfrac{2}{3}\alpha^{-2}=1.25\times10^4, \tag{11}$$

yielding the extremely large and narrow resonance cross section. This value would be reduced and broadened if other broadening mechanisms were operative. We shall not pursue this further since the results will depend upon the experimental environment of the atom. An analytic continuation of (10) to the region above the first threshold can be obtained by an integration by parts, reducing the power of the singularity in the integrand.

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[3] This result has been obtained previously by Professor C. Schwartz (unpublished). We are indebted to him for making it available to us and for his instructive comments.

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# Study of Electron Correlation in Helium-Like Systems Using an Exactly Soluble Model*

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The exact solution of a two-electron system in which the electron-electron interaction is Coulombic but the electron-nuclear attraction is a harmonic oscillator potential gives the following wave function: $\chi_1\chi_2 f(r_{12})$, where the $\chi$'s are one-particle spherical harmonic oscillator wave functions. The exact $f(r_{12})$ has only a small curvature in $r_{12}$, the distance between the two electrons. This exactly soluble model is used to gain some insight into electron correlation in actual two electron atoms and into the usual approximations. A variational trial function, $f(r_{12})=1+\alpha r_{12}$, where $\alpha$ is a variable parameter, gives energies and even wave functions close to the exact solution. The correlation energy determined from an analytic Hartree-Fock solution and the average angle between the two electrons are somewhat less than in actual helium-like systems.

## I. INTRODUCTION

FROM the early work of Hylleraas to the present, the main problem in the quantum mechanics of two-electron systems has been the choice of correct trial wave functions. The present state of this research is summarized by Löwdin.[1] The problem is to find the correct two-electron part of the wave function since the Hartree-Fock solution is the best one-electron result.

The studies of Fock,[2] Kinoshita,[3] Kato,[4] and others sought to obtain the form of a power series solution, hoping that a trial function of that form would rapidly converge to the exact wave function. Kinoshita's energy calculations on helium[3] attest to this approach.

However, one cannot solve the two-electron atomic system exactly; nor can one obtain the coefficients of each term in a formal power series solution. To study the two-electron effects which represent the correlation in the motions of the two electrons, we consider here a model problem which can be solved exactly.

A single-particle Gaussian wave function of a spheri-

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† National Science Foundation Predoctoral Fellow.

[1] P. O. Löwdin, in *Advances in Chemical Physics,* edited by I. Prigogine (Interscience Publishers, Inc., New York, 1959), Vol. II, p. 207; P. O. Löwdin and L. Redei, Phys. Rev. **114**, 752 (1959).

[2] V. Fock, Kgl. Norske Videnskab. Selskabs Forh. **31**, 138, 145 (1958).

[3] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).

[4] T. Kato, Trans. Am. Math. Soc. **70**, 195, 212 (1951).

cally symmetric harmonic oscillator is quite similar to the 1*s* state of a hydrogenic atom, lacking primarily a cusp at the origin. Our model consists of *two electrons placed in a harmonic oscillator well, but repelling one another with the Coulomb force.* Since the electron-electron interaction is the same as in actual helium atom and only the nuclear attraction is approximated, the model is realistic as far as electron correlation is concerned.

Even the analogous model for the hydrogen molecule can be solved, but the behavior of the harmonic oscillator potential at long distances makes this a poor approximation.

Similar models have been used in the study of nuclei.[5] On finite nuclei, Eden and Emery[6] used single-particle harmonic oscillator potentials and effective pairwise nucleon interactions treating the hard core as a perturbation. Our model combined with that of Eden and Emery may be useful in calculating electrostatic repulsion effects in finite nuclei.

Gaussian orbitals have been used also in actual atomic and molecular problems as infinite basis sets for the correct Hamiltonian.[7,8] They are easier to use than exponentials in regard to the evaluation of integrals. Two-electron systems were studied this way by Kimball and Neumark.[9] Single Gaussians used as trial functions with the true Hamiltonian give poor energy values in atomic systems primarily due to the lack of a cusp at the origin. The sum of two Gaussians is somewhat better[8] because they tend to create a cusp. The studies all use Gaussians to build up convenient trial functions for the true Hamiltonian. They are of a different nature than the work reported here with a model Hamiltonian.

Wulfman[10] also studied a model, but he replaced all Coulombic interactions, including electron-electron repulsions, by harmonic oscillator potentials in his study of large molecules.

Our purpose is to study the correlation part of the wave function and energy with the model defined above. Correlation energies of two-electron systems are remarkably insensitive to central fields (e.g., they change very little along the He, $\mathrm{Li}^+$, $\mathrm{Be}^{++}$ isoelectronic series[1]). Therefore, a model in which the $(1/r_{12})$ repulsion is retained as such and only the nuclear attractions replaced should be a useful one. Most of the specifics of the electron-electron interaction should appear in the two-electron part of the wave function and this should be closely related to real atomic systems. We shall compare the exact solution of this model with trial functions similar to those used on actual two-electron atoms.

One of us[11] has shown how the main part of the correlation in a many-electron atom can be obtained from those of two-electron systems in a Hartree-Fock "sea." Methods similar to those of Hylleraas can be used on these so that detailed study of correlation in two-electron systems acquires added significance.

## II. EXACT SOLUTION

With nuclear attractions in an actual two-electron atomic system replaced by harmonic oscillator potentials, the Hamiltonian of the model is

$$\mathcal{H}=-(\hbar^2/2m)(\nabla_1^2+\nabla_2^2)+\tfrac{1}{2}k(r_1^2+r_2^2)+(e^2/r_{12}). \tag{1}$$

Distances $r_1$ and $r_2$ are from the nucleus to electrons one and two, respectively. $\nabla_1^2$ and $\nabla_2^2$ are the Laplacians of the two electrons. $k$ is the effective force constant of our oscillator composed of an electron and the nucleus; $m$ is the reduced mass of each electron. $r_{12}$ is the distance between the electrons, $|\mathbf{r}_2-\mathbf{r}_1|$. Cartesian coordinates centered on the nucleus are $x_1$, $y_1$, $z_1$ for electron one and $x_2$, $y_2$, $z_2$ for electron two.

We perform the following coordinate transformations:

$$\begin{aligned} &X_1=(x_1+x_2)/2, \quad Y_1=(y_1+y_2)/2, \quad Z_1=(z_1+z_2)/2;\\ &X_2=x_2-x_1, \qquad Y_2=y_2-y_1, \qquad Z_2=z_2-z_1. \end{aligned} \tag{2}$$

The transformed equation,

$$\mathcal{H}\Psi(X_1,Y_1,Z_1,X_2,Y_2,Z_2)=E\Psi \tag{3}$$

(where $\Psi$ is the total wave function and $E$ is the total energy), is separable:

$$\Psi=\Phi(X_2,Y_2,Z_2)\Gamma(X_1,Y_1,Z_1), \tag{4}$$

with

$$-\frac{\hbar^2}{4m}\left(\frac{\partial^2\Gamma}{\partial X_1^2}+\frac{\partial^2\Gamma}{\partial Y_1^2}+\frac{\partial^2\Gamma}{\partial Z_1^2}\right)+k(X_1^2+Y_1^2+Z_1^2)\Gamma=E_\Gamma\Gamma, \tag{5}$$

and

$$-\frac{\hbar^2}{m}\left(\frac{\partial^2\Phi}{\partial X_2^2}+\frac{\partial^2\Phi}{\partial Y_2^2}+\frac{\partial^2\Phi}{\partial Z_2^2}\right)+\frac{k}{4}(X_2^2+Y_2^2+Z_2^2)\Phi+\frac{e^2\Phi}{(X_2^2+Y_2^2+Z_2^2)^{\frac{1}{2}}}=E_\Phi\Phi, \tag{6}$$

where

$$E_\Gamma+E_\Phi=E. \tag{7}$$

The solution of Eq. (5) is that of a spherically sym-

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[5] D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961), pp. 12–13; Y. C. Hseih and I. Block, Phys. Rev. **101**, 205 (1956); G. A. Baker, Jr., J. L. Gammel, B. J. Hill, and J. G. Wills, Phys. Rev. **125**, 1754 (1962).

[6] R. J. Eden and V. J. Emery, Proc. Roy. Soc. (London) **A248**, 266 (1958).

[7] S. F. Boys, Proc. Roy. Soc. (London) **A200**, 542 (1950); R. K. Nesbet, J. Chem. Phys. **32**, 1114 (1960).

[8] R. McWeeny, Nature **166**, 21 (1950); Acta Cryst. **6**, 631 (1953).

[9] G. E. Kimball and G. F. Neumark, J. Chem. Phys. **26**, 1285 (1957).

[10] C. E. Wulfman, J. Chem. Phys. **33**, 1567 (1960).

[11] O. Sinanoḡlu, J. Chem. Phys. **36**, 706 (1962); Proc. Natl. Acad. Sci. U. S. **47**, 1217 (1961); Proc. Roy. Soc. (London) **A260**, 379 (1961).

metric harmonic oscillator of force constant $4k$[12]:

$$\Gamma=\exp[-(km)^{1/2}r_+^2/\hbar]r_+^l Y_{lm}(\theta,\phi)G(r_+^2), \quad (8)$$

where $G(r_+^2)$ is a confluent hypergeometric function,

$$r_+^2=X_1^2+Y_1^2+Z_1^2, \quad (9)$$

and $Y_{lm}(\theta,\phi)$ are the spherical harmonics. In the ground state $l=0$, $Y_{00}$ and $G$ are constants, and

$$E_\Gamma=\tfrac{3}{2}\hbar(k/m)^{1/2}. \quad (10)$$

The solution of Eq. (6) is more complicated. Treating only the ground state (most symmetric case), the angular part of the wave function is a constant. If $r_{12}^2=x_2^2+y_2^2+z_2^2$, we get

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\Phi}{\partial r_{12}^2}+\frac{2}{r_{12}}\frac{\partial\Phi}{\partial r_{12}}\right]+\frac{k}{8}r_{12}^2\Phi+\frac{e^2\Phi}{2r_{12}}=\frac{E_\Phi}{2}\Phi. \quad (11)$$

We remove the first derivative term by the transformation $\Phi=\nu/r_{12}$ and put our equation in dimensionless form, setting

$$r_{12}=[2\hbar/(mk)^{\frac{1}{2}}]^{\frac{1}{2}}\eta,$$

$$\frac{d^2\nu}{d\eta^2}=\left(\eta^2+\frac{\beta}{\eta}-\epsilon\right)\nu, \quad (12)$$

where energy $\epsilon$ is in oscillator units: $E_{\text{osc}}\equiv(\hbar/2)(k/m)^{1/2}$; and $\beta=(E_{\text{au}}/E_{\text{osc}})^{1/2}$; $E_{\text{au}}$ is the atomic unit of energy (twice the energy of the hydrogen atom, 27.21 eV).

The eigenvalues of this equation cannot be found by standard Frobenius power series methods[13] since we have an irreducible three term recursion formula. Thus we are forced to a numerical procedure.[14]

$\beta$ represents the strength of the electron-electron repulsion compared to nuclear attraction. It should decrease with increasing nuclear charge. To get a specific value for $\beta$, we use a Gaussian orbital as a trial function on an actual hydrogen-like atom. The force constant is the variable parameter. Doing this, McWeeny[8] found

$$k=(4m^3e^8Z^4/\hbar^6)(8/9\pi)^2,$$

or

$$E_{\text{osc}}=(\hbar/2)(k/m)^{1/2}=(me^4Z^2/\hbar^2)(8/9\pi)=E_{\text{au}}(8/9\pi)Z^2.$$

Therefore

$$\beta=(9\pi/8Z^2)^{1/2}=1.879970/Z. \quad (13)$$

Once $\beta$ is chosen and the model thereby related to the actual atom, the problem becomes the solution of Eq. (12) to obtain the exact wave function of the model. The zero of energy differs from that in a real atom since our potential is zero at the "nucleus," whereas in an actual atom the potential is zero at infinite distance from the nucleus. For this reason our energies are positive, and not negative as in real atoms.

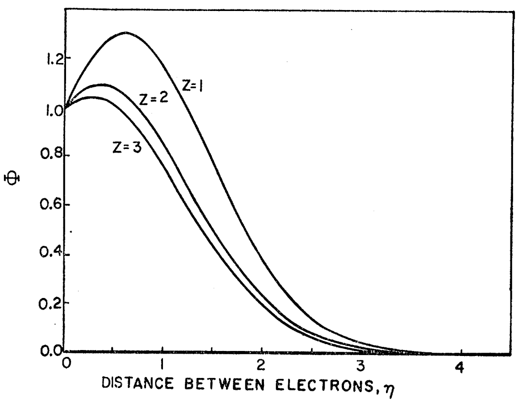

FIG. 1. Wave functions, $\Phi(r_{12})$, vs effective atomic number, $Z$.

Initial estimates of these wave functions and the eigenvalues were obtained by hand computation. Further refinements were done on the IBM-709 computer of Yale University. The integrations from $\eta=0$ to $\eta=4.0$ (outward) are very sensitive to the eigenvalue at long distances. Following Hartree,[15] inward integrations were performed starting at $\eta=7.0$ and matched to the outward integrations at $\eta=3.3$. Hartree's method for initiating the inward integration was used.[15]

In Fig. 1 the wave function $\Phi$ is plotted for $Z=1$, 2, and 3 in terms of $\eta$. The curves are adjusted to intersect at one for $\eta=0$. To convert the abscissa to Bohr radii, $\eta$ is multiplied by $\beta$. The exact energies are listed in Table I. The total energy is the sum of Eq. (10) and the numerical solution eigenvalue. Errors in energy were independently estimated from the mismatch in the inward and outward integrations.[15]

More meaningful is $[\Phi/e^{-\eta^2/2}]=f(r_{12})$ since this represents the deviation of $\Psi$ from the uncoupled oscillator results [$e=0$ in Eq. (1)]. In Fig. 2 we plot $f(r_{12})$ in terms of $\eta$. The solution up to $\eta=6$ is the numerical solution (inward and outward integrations).

If we let $He^{-\eta^2/2}=\nu$, we get

$$(d^2H/d\eta^2)-2\eta(dH/d\eta)+[\epsilon-1-(\beta/\eta)]H=0. \quad (13b)$$

Notice that $f(r_{12})=H/\eta$. The power series solution is

$$f(r_{12})=1+(\beta/2)\eta+\sum_{m=2}^{\infty}a_m\eta^m. \quad (14)$$

$$a_{m+1}=[\beta a_m+(2m+1-\epsilon)a_{m-1}]/(m+1)(m+2). \quad (15)$$

This is a convergent alternating series for large $m$. It converges very slowly and is useless beyond about $\eta=1.5$.

The asymptotic solution[16] of Eq. (13b) is more inter-

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[12] E. Landau and E. Lifshitz, *Quantum Mechanics: Nonrelativistic Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 129–30.

[13] J. Irving and N. Mullineux, *Mathematics in Physics and Engineering* (Academic Press Inc., New York, 1959), p. 69.

[14] Reference 13, p. 697.

[15] D. Hartree, *Calculation of Atomic Structures* (John Wiley & Sons, Inc., New York, 1957), pp. 82–84.

[16] J. Irving and N. Mullineux, reference 13, pp. 102–103.

TABLE I. Energy[a] calculations for two electrons in an harmonic oscillator well, with a trial function given by $(e^{-\delta_1\rho_1^2/2}+Be^{-\delta_2\rho_1^2/2})(e^{-\delta_1\rho_2^2/2}+Be^{-\delta_2\rho_2^2/2})f(r_{12})$, where $f(r_{12})=1+\alpha\eta=1+(\alpha/\sqrt{2})\rho_{12}$.

| Calculation | $H^-$ ($Z=1$) | He ($Z=2$) | $Li^+$ ($Z=3$) |
|---|---|---|---|
| Exact solution of model | $7.8919_4$ | 6.99800 | $6.6783_8$ |
| Single orbitals ($\alpha=0$, $\delta_1=1.0$, $B=0$) | 8.1214 | 7.0607 | 6.7071 |
| Screened orbitals ($\alpha=0$, $B=0$) (simplest analytic Hartree-Fock) | 8.0352 ($\delta_1=0.850$) | 7.03822 ($\delta_1=0.918$) | 6.6970 ($\delta_1=0.945$) |
| Two-term Gaussian orbitals ($\alpha=0$) (analytic Hartree-Fock) | $7.9983_0$ ($\delta_1=0.920$, $\delta_2=3.4_0$, $B=-0.24_0$) | 7.02857 ($\delta_1=0.95_3$ $\delta_2=3.8_5$, $B=-0.13_0$) | $6.6926_6$ ($\delta_1=0.96_8$, $\delta_2=4.5_0$, $B=-0.08_3$) |
| Linear variation function ($\delta_1=1.0$, $B=0$) | 7.8920 ($\alpha=0.8994$) | 6.99863 ($\alpha=0.3320$) | 6.6789 ($\alpha=0.2017$) |

[a] Oscillator unit of energy $E_{\text{osc}}=\frac{1}{2}\hbar(k/m)^{1/2}$ (see text). The zero of energy is such that the harmonic oscillator potentials are zero at the "nuclei." [See remarks after Eq. (13).] The potential is always positive.

esting and useful:

$$f(r_{12})\sim\eta^{(\epsilon-3)/2}\left[1+\frac{\beta}{2\eta}+\sum_{m=2}^{\infty}b_m\eta^{-m}\right], \tag{16}$$

$$b_m=[4\beta b_{m-1}-(2m-3-\epsilon)(2m-1-\epsilon)b_{m-2}]/8m. \tag{17}$$

This series does not converge, common for most asymptotic expansions,[17] but often it can be truncated to give a good estimate of the function. In our case four to six terms of Eq. (16) give results good to four decimal places even for $\eta=2.0$.

The form of Eq. (16) is quite as expected. If our oscillators were uncoupled ($\beta=0$), we would have $\epsilon=3.0$ and our final $f(r_{12})$ would be unity for all $\eta$ ($b_m=0$ for all $m>0$). In that case the $H$'s are Hermite polynomials. The $\eta^{(\epsilon-3)/2}$ term is the same for any potential, $V=r_{12}^{-n}$ where $n>0$.

In Table II we list the coefficients in Eq. (16) for $Z=1$, 2 and 3. These solutions are plotted in Fig. 2 as a continuation of $f(r_{12})$ beyond $\eta=5.0$. Actually the solution of Eq. (16) holds down to about $\eta=1.0$ and compares well with both the numerical and power series solutions Eq. (14) where each is applicable. The numerical solution is the least accurate due to matching and accumulated errors.

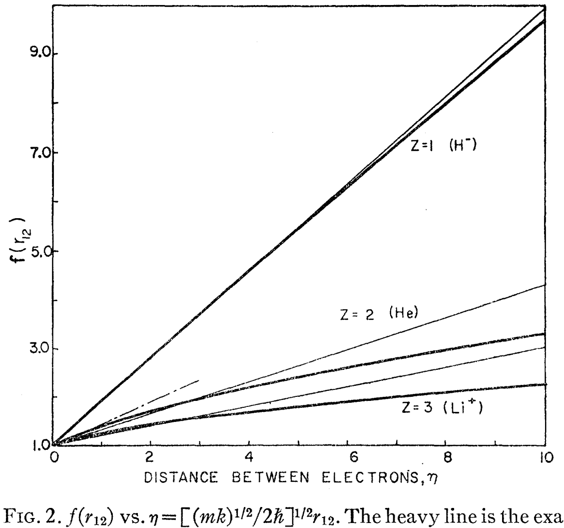

FIG. 2. $f(r_{12})$ vs. $\eta=[(mk)^{1/2}/2\hbar]^{1/2}r_{12}$. The heavy line is the exact solution; the light line is the variational solution, $f(r_{12})=1+\alpha r_{12}$; and the broken line is the initial slope of the exact solution for the helium-like case. Outward integrations: $\eta=0$ to 3.3; inward integrations: $\eta=3.3$ to 7.0; power series: $\eta=0$ to 1.0; asymptotic series: $\eta>2$.

The final wave function is

$$\Psi=f(r_{12})\exp\{[-(km)^{1/2}/2\hbar](r_1^2+r_2^2)\}. \tag{18}$$

with $f(r_{12})$ behaving almost linearly with respect to $r_{12}$. In Fig. 3 the total energy is plotted versus $\beta$ and we find it is almost linear in it. Fitting our exact eigenvalues, the energy can be expressed as a rapidly convergent power series in $\beta$:

$$E=6+1.1277\beta-0.07588\beta^2+0.00603\beta^3, \tag{19}$$

where $E$ is in oscillator units, Eq. (13). This result will be compared later with the energy of He-like ions as a function of $Z$. The energy in Eq. (19) is positive for reasons explained after Eq. (13).

## III. COMPARISON WITH VARIATIONAL SOLUTIONS

Since $f(r_{12})$ is almost linear in $\eta$ or $r_{12}$, a useful form of trial function[1] is

$$\Psi_{\text{trial}}=(e^{-\delta_1\rho_1^2/2}+Be^{-\delta_2\rho_1^2/2})\times(e^{-\delta_1\rho_2^2/2}+Be^{-\delta_2\rho_2^2/2})(1+\alpha'\rho_{12}), \tag{20}$$

using dimensionless variables

$$[\rho=(mk/\hbar^2)^{1/4}r,\ E_T=\tfrac{1}{2}\hbar(k/m)^{1/2}\epsilon_T].$$

Notice that the distance units are not those of Eq. (12) due to the symmetry of the coordinate transformation, Eq. (2), e.g., $\alpha'=\alpha/\sqrt{2}$.

TABLE II. Six coefficients in the asymptotic expansion of $f(r_{12})$, using Eq. (16): $f(r_{12})=\eta^{(\epsilon-3)/2}\sum_{m=0}^{\infty}b_m\eta^{-m}$.

| | $Z=1$ | $Z=2$ | $Z=3$ |
|---|---|---|---|
| $b_0$ | 1.00000 | 1.00000 | 1.00000 |
| $b_1$ | 0.93999 | 0.46999 | 0.31333 |
| $b_2$ | −0.01842 | −0.07655 | −0.06447 |
| $b_3$ | 0.00224 | 0.00759 | 0.00497 |
| $b_4$ | 0.00066 | 0.00809 | 0.00923 |
| $b_5$ | −0.00036 | −0.00209 | −0.00162 |
| $(\epsilon-3)/2$ | 0.94597 | 0.49900 | 0.33919 |

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[17] E. D. Rainville, *Special Functions* (The Macmillan Company, New York, 1960), p. 33.

Substituting Eq. (20) into the standard variational formula and minimizing the energy with respect to the $\delta$'s or $\alpha'$; various special cases were treated. The resulting parameters and energies are listed in Table I. The case of $\alpha'=0$, $\delta_1=1$, $B=0$ gives simply the Coulombic interaction of two independent oscillator orbitals. The solutions for $\alpha'=0$ correspond to various approximations to the Hartree-Fock result. The case where $B$ is not zero is known to be a good analytic representation to the Hartree-Fock orbitals from studies on the corresponding atomic cases.[1]

The $f(r_{12})$ determined by variational methods are plotted in Fig. 2 and we see that this simple function does fit the exact result quite well.

## IV. DISCUSSION AND COMPARISON WITH ACTUAL TWO-ELECTRON SYSTEMS

The most significant feature of the correlation function $f(r_{12})$ is the almost linear behavior. The assumption, $f(r_{12})=1+\alpha r_{12}$ is very good energywise and is also quite close to the true correlation function. For $Z=2$ (He-like model) the error in the exact energy of the model due to using this trial function is only 0.00071 a.u. (0.019 eV). This linear form of the wave function is called a "correlated orbital"[1]

$$\chi_1\chi_2(1+\alpha r_{12}), \tag{21}$$

where $\chi_1$ and $\chi_2$ are one-electron wave functions. Hylleraas[18] was the first to notice that this form improves the energy significantly beyond any one-electron wave functions despite their simplicity. For the helium case he found $\alpha=0.364$ using screened Slater orbitals compared to our $\alpha=0.353$ (in reciprocal Bohr radii). This method is also useful in many-electron atoms.[11] Notice that most of the difference between Coulombic and harmonic potentials is in the one-electron part $(\chi_1\chi_2)$.

Equation (21) gives good energies for actual helium-like ions only when the trial function is "scaled" to satisfy the virial theorem.[1] In our model, the standard virial theorem no longer applies since our potential is a mixture of harmonic oscillator and Coulombic interactions. The $f(r_{12})=1+\alpha r_{12}$ without any modification gives a much better energy (within 0.02 eV) on the model than even the "scaled" trial function does on actual ions (within *ca* 0.2 eV). This is due, in part, to the lack of a cusp in the oscillator wave function, and the difference in the behavior of the two parts of the potential at long distances. How well the linear form gives the correct energy depends on two factors:

(a) The larger the value of $Z$, the closer crude wave functions give the correct energy in two-electron systems.

(b) The smaller the value of $Z$, the closer the exact $f(r_{12})$ is to a linear form [see Eq. (16)]. Therefore the energy will be better also.

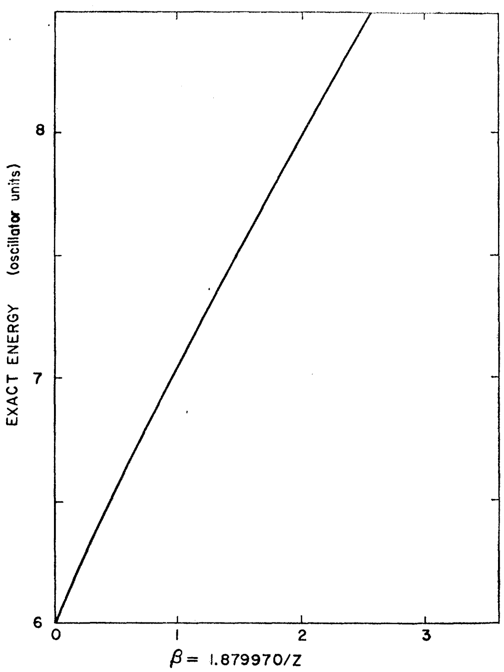

FIG. 3. Total energy vs coupling parameter $\beta$.

These two factors explain the observed trends in these energy differences in Table I and in real atoms.

Our exact solution [Eq. (14)] in a power series has the same form as Slater[19] obtained for two electrons so far from the nucleus of a helium atom that one can treat the nuclear attraction as a constant. He finds

$$f(r_{12})=1+\tfrac{1}{2}r_{12}+\cdots, \tag{22}$$

or in oscillator units

$$f(r_{12})=1+\tfrac{1}{2}\beta\eta+\cdots. \tag{23}$$

The first two terms are the same as in our model [Eq. (14)]. However, the complete power series solution converges very slowly and is useless beyond about $\eta=1.5$. This constant factor in front of $\eta$ is quite different from that which yields the best value of the energy by variational calculation (see Fig. 2).

We can also compare our exact solution (Fig. 2) with plots of Kinoshita's thirty-eight term wave functions vs $r_{12}$ for various $r_1+r_2$ and $r_2-r_1$ values.[19] Both have the same shape. Notice also that our wave function is exact to all distances whereas any variational solution, since it is concerned primarily with the most important parts of the wave function, is expected to be increasingly poor at long distances.

Actually $f(r_{12})$ is not the true correlation function since it is not independent of (orthogonal to) the single-electron part. It is the orthogonal part which is physically meaningful. Details of the true correlation func-

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[18] E. A. Hylleraas, Z. Physik **65**, 209 (1930).

[19] J. C. Slater, *Quantum Theory of Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II, pp. 37–39. See also Kato's work in reference 3.

TABLE III. Correlation energies.

| | Actual atom[a] (eV) | Our model (eV) |
|---|---|---|
| Hydride ion ($Z=1$) | $-1.08$ | $-0.819$ |
| Helium atom ($Z=2$) | $-1.142$ | $-0.941$ |
| Lithium ion ($Z=3$) | $-1.182$ | $-0.989$ |

[a] P. O. Löwdin, reference 1, p. 240.

tions in real two-electron systems and their effect on the original orbitals are discussed by Sinanoğlu and Tuan.[20]

For two-electron atomic systems, Hylleraas and Midtdal[21] give the energy as a function of the atomic number, $Z$:

$$E\ (\text{in atomic units}) = -Z^2+\tfrac{5}{8}Z-0.15765 + \frac{0.00854}{Z} - \frac{0.00034}{Z^2} - \frac{0.00082}{Z^3} - \frac{0.00245}{Z^4}. \qquad (24)$$

Using our energy expression Eq. (19), we get

$$E(\text{a.u.}) \cong 3.53429Z^2+0.59985Z -0.07588+0.01133/Z. \qquad (25)$$

The signs of the first terms in Eqs. (24) and (25) differ because they have different zeros of energy [see remarks following Eq. (13)]. Terms beyond the first in each case represent the effects of electron-electron interaction.

The total energy in our model is not expected to agree with the energy of an actual two-electron system, Eq. (24), since our Hamiltonian is different. We really want to compare the correlation energies defined as the difference between the exact eigenvalue and the Hartree-Fock expectation value of a given Hamiltonian.[1] Since the Hartree-Fock wave functions are the best possible one-electron functions, the correlation energy is a measure of electron-electron interactions over and above any average interaction. From remarks made in the Introduction, we expect that most of the specifics of the nuclear attraction will be absorbed in the one-electron part of the wave functions, leaving correlation energies similar to those in actual atoms.

The trial function, Eq. (20), with $\alpha'=0$ minimized with respect to the other three parameters is a good approximation to the Hartree-Fock wave function and energy of the model. The analogous function in real two-electron systems reproduces the Hartree-Fock functions to three significant figures.[1] The correlation energies for our model are the difference between the exact numerical solutions of Sec. II and the two-term Gaussian analytic Hartree-Fock solution discussed above. Correlation energies for our model and for actual two-electron atomic systems are listed in Table III. The correlation energies for our model are within 0.26 eV of those in actual systems. This difference is probably due to the mixed potential in our model; the Coulombic part decreasing with increasing distance, while the oscillator force increases. The lack of a cusp in the wave function also reduces correlation energies.

It is also of interest to compare the average angle between the two electrons in our model with the angle in an actual atom. The average of the cosine of the angle between the two electrons is easily calculated using

$$\cos\theta_{12} = (r_1^2+r_2^2-r_{12}^2)/2r_1r_2. \qquad (26)$$

For $\alpha=0$, i.e., no correlation effects in the wave function, $\theta_{12}=90°$. Using trial function, Eq. (20), with $B=0$, $\delta_1=1.0$ and integrating over all space, one gets

$$\text{He}:\quad \theta_{12}=92.0°,$$
$$\text{Li}^+:\quad \theta_{12}=91.3°,$$
$$\text{H}^-:\quad \theta_{12}=97.3°.$$

Lennard-Jones and Pople,[22] using a wave function expanded in terms of Legendre polynomials in $\cos\theta_{12}$, calculated a maximum angle of 96° and an average angle of 93.8° for helium.

## V. CONCLUSION

The object of this paper was to compare the exact two-electron part of the wave function with the usual type of trial functions using a model system. We found that $(1+\alpha r_{12})$ with $\alpha$ determined variationally is a good approximation over the entire range of $r_{12}$ since the curvature of the exact two-electron part of the wave function is small.

We also compared correlation energies and the average angle between the two electrons in our model with actual values. They were somewhat lower.

The exact solution on a model where the electron-electron interaction is realistic gives considerable insight into the correlation behavior of actual two-electron atomic systems.

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