

Importance of Angular Correlations between Atomic Electrons*

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(Received December 4, 1961)

We present the results of some new calculations on two atomic problems—the correlation energy in the ground state of 2-electron atoms, and elastic scattering of slow electrons from hydrogen atoms—to show the relative importance of various angular components of the complete wave function. We conclude that, as a general rule, the use of just (relative) s and p waves will give quite accurate answers—with only a few percent errors at most; but to obtain higher precision one should abandon the Legendre polynomial expansion and use the coordinate r_{12} .

I. INTRODUCTION

THE central-field approximation is certainly a good starting point for most atomic problems; it is necessary now to obtain a thorough understanding of the finer effects brought on by the working of the interelectron Coulomb repulsion energy e^2/r_{12} . The well-known Hartree approximation takes the spherical average of this interaction and thus allows for only some radial correlation in the wave function. This method often gives quite satisfactory answers, and its goodness (we shall not dwell on the virtue of its simplicity) is easily attributed to the long-range nature of the force. Yet e^2/r_{12} does have a singularity at small separations and this implies some important contributions from states of large relative-angular momentum. The schemes for improving the Hartree results are generally described as “superposition of configurations.”

At the extreme of accuracy are the results of variational calculations, initiated by Hylleraas, using functions of the interelectron separation r_{12} in the wave function. The realm between these two methods has not until now been well understood—a number of previous attempts are discussed and criticized in Sec. IV. In this paper we present the results of some restricted variational calculations on two famous problems, along with some semiquantitative mathematical analysis, which provides a basis for evaluating the relative merits of these different approaches.

II. SECOND-ORDER ENERGY IN TWO-ELECTRON ATOMS

The complete problem of the two-electron atom is too complicated for the analysis we desire to carry out, so we discuss instead the case where the central field is strong and expand in inverse powers of Z . For the ground state we have the well-known terms

$$E = +(e^2/a_0)(-Z^2 + \frac{5}{8}Z + E_2 + \dots), \quad (1a)$$

$$\psi = \psi_0 + \psi_1/Z + \dots, \quad (1b)$$

where ψ_0 is the $(1s^2)$ state of hydrogen. The remaining

interesting quantities are frequently expressed in terms of infinite sums

$$E_2 = \sum_n \left| \left\langle 0 \left| \frac{e^2}{r_{12}} \right| n \right\rangle \right|^2 / (E_0 - E_n), \quad (2a)$$

$$\psi_1 = \sum_n \left| n \right\rangle \left\langle n \left| \frac{e^2}{r_{12}} \right| 0 \right\rangle / (E_0 - E_n). \quad (2b)$$

While E_2 (or ψ_1) has never been exactly evaluated, very accurate approximations have been obtained by use of the variational expression

$$E_2 \leq [E_2] = 2\langle \psi_0 | e^2/r_{12} | \psi_1 \rangle - \langle \psi_1 | E_0 - H_0 | \psi_1 \rangle. \quad (3)$$

Using a trial function of the form

$$\psi_1 = \psi_0 \sum C_{pq} r_{12}^p (r_1 - r_2)^q (r_1 + r_2)^r, \quad (4)$$

Hylleraas and Midtdal¹ obtained the value $[E_2] = -0.157658$ [in atomic units (a.u.) $e^2 = a_0 = 1$]; and we have extended this work to get (with 70 terms) $[E_2] = -0.157663$ which we believe is within 0.000003 of the correct value. We are not interested here in the value of E_2 *per se*, but we shall use it to measure the goodness of some approximate calculations to be described.

The Coulomb interaction between the electrons may be expanded as

$$e^2/r_{12} = e^2 \sum_{l=0}^{\infty} P_l(\cos\theta) r_1^l / r_2^{l+1}, \quad (r_1 < r_2), \quad (5)$$

where θ is the angle between the two position vectors. For each term in (5) the contributing terms $|n\rangle$ in (2) must also have the angular structure given by $P_l(\cos\theta)$, and we may study separately the angular components of ψ_1 or E_2 ,²

$$E_2 = \sum_{l=0}^{\infty} E_2(l). \quad (6)$$

The central problem we wish to study is the relative magnitudes of the terms of (6).

* Supported in part by the Advanced Research Projects Administration through the U. S. Office of Naval Research, and in part by the U. S. Atomic Energy Commission and by the United States Air Force under grant AF-AFOSR 62-121 monitored by the Air Force Office of Scientific Research of the Air Research and Development Command.

¹ E. A. Hylleraas and J. Midtdal, Phys. Rev. **103**, 829 (1956); **109**, 1013 (1958).

² It was in order to achieve this separation that we chose to study the second-order energy, and not the complete energy.

If we delete all terms containing r_{12} from the wave function (4), we can then carry out a variational calculation for $E_2(0)$. The result we get for this truncated calculation is³

$$E_2(0) = -0.12527 \pm 0.00005.$$

Then, allowing terms with r_{12}^2 as well, we can carry out a variational calculation for the $l=0+l=1$ parts of E_2 , then by subtraction

$$E_2(1) = -0.0263 \pm 0.0002.$$

The first significant result is that the relative s wave alone gives 80% of the total and the s -plus- p waves give 96% of the total second-order energy. Now we turn to the higher l contributions.

Since the above subtraction procedure involves a growing loss of accuracy, we attempted a direct attack using trial functions,

$$\psi_1(l) = \psi_0 P_l(\cos\theta) r_1^l r_2^l \sum C_{qr} (r_1 - r_2)^q (r_1 + r_2)^r, \quad (7)$$

with the following results [with up to 30 terms in (7)]:

$$\begin{aligned} E_2(2) &< -0.0034, \\ E_2(3) &< -0.00068, \\ E_2(4) &< -0.00009. \end{aligned} \quad (8)$$

The obvious remark to be made about these results is that they cannot be very close to the correct values since they add up to only about $\frac{2}{3}$ of the difference between the complete E_2 and its $s+p$ parts. If the numbers (8) are given any credence, one is led to the conclusion that the expansion (6) is rapidly convergent (a number of people have drawn this conclusion from calculations similar to ours just described—see Sec. IV); this conclusion is false.

A closer inspection of our calculations shows that the additional contributions to $E_2(l)$ with addition of more terms in (7) do not decrease rapidly, this situation becoming more unpleasant for the higher l values. This poor convergence may be understood by examining the behavior of the perturbing term from (5). This function is strongly peaked around the point $r_1 = r_2$ and falls off with the l th power of the distance away from this point. It may be inferred that the function $\psi_1(l)$ should therefore also have a sharply varying structure in this region; but the trial functions used are individually smooth, and therefore a great many terms will be required for an accurate representation.

It is possible to carry out this analysis more precisely by considering the differential equation which defines ψ_1 :

$$(E_0 - H_0)\psi_1 = (e^2/r_{12})\psi_0. \quad (9)$$

Focusing on the region near $\mathbf{r}_1 = \mathbf{r}_2$, it is easily seen that

the important part of this equation is just

$$-\frac{1}{2} \frac{\hbar^2}{2m} (\nabla_1 - \nabla_2)^2 \psi_1 = \frac{e^2}{r_{12}} \psi_0, \quad (9a)$$

and the solution of this simplified equation yields our leading approximation

$$\psi_1 \approx (r_{12}/2a_0)\psi_0, \quad (10)$$

then integrating over angles with the factor $P_l(\cos\theta)$, we get

$$\psi_1(l) \approx \frac{P_l(\cos\theta)}{2a_0} \psi_0 \frac{r_{<}^l}{r_{>}^{l+1}} \left[\frac{r_{<}^2}{2l+3} - \frac{r_{>}^2}{2l-1} \right]. \quad (11)$$

If we set $r_{<} = r_{>}(1-\delta)$, this function is approximated by (for large l and small δ)

$$-(r/2a_0 l^2) e^{-\delta l} (1+\delta l) \psi_0 P_l(\cos\theta), \quad (12)$$

which is peaked around $r_1 = r_2$ and falls off rapidly outside a distance

$$|(r_1 - r_2)/r_1| \sim l^{-1}.$$

We can now see two reasons why attempts to represent $\psi_1(l)$ for large l values by sums of product functions $u(r_1)v(r_2)$ will be very slowly convergent. First, is the very strong radial correlation described by the sharp peaking of the function (11); second, is the fact that this function has a (finitely) discontinuous third derivative, and thus its second derivative, which appears in the variational principle, is a function with a cusp.

The expression (11) can be put into the variational principle for $E_2(l)$ with a variable coefficient λ_l . This will give an upper bound on the true values, and we have calculated the result⁴

$$-E_2(l) \geq (45/256)l^{-4}, \quad (\text{for } l \gg 1). \quad (13)$$

Because of the above arguments about the peaking at $r_1 = r_2$, supported by the result that

$$\lambda_l \xrightarrow{l \rightarrow \infty} 1,$$

we believe that (13) is actually the correct asymptotic result. We now state our second significant result: Attempts to improve on the $s+p$ -wave results by the addition of higher l terms will be at best only slowly rewarding: Particular attention must be given to the strong radial correlation of the higher l functions.

In contrast with this discouraging outlook for the Legendre polynomial expansion, we claim that the Hylleraas terms—odd powers of r_{12} as well as the even ones—are the right functions to use for high-accuracy calculations. The results of our first-mentioned calculation of E_2 converged quite rapidly (see Table I), at

³ C. W. Scherr, J. Chem. Phys. **33**, 317 (1960), has attempted a direct summation of (2a) and finds $E_2(0) = -0.13362$, $E_2(1) \geq -0.0103$, $E_2 \geq -0.14392$. We believe there is an error in his $l=0$ result.

⁴ The details of this calculation will be given as part of a general analysis of rates of convergence in an article to be published in *Computational Methods in the Physical Sciences*, edited by Alder, Fernbach, and Rotenberg (Academic Press Inc., New York, 1962), Vol. 1.

TABLE I. Calculations of the second-order energy (in a.u.) using Hylleraas-type functions.

Maximum of ($p+q+r$)	No. of terms in (4)	$[E_2]$	Differences	Ratios of differences
1	3	-0.1461338		
2	7	-0.1566022	-0.0104684	0.080
3	13	-0.1574400	-0.0008378	0.198
4	22	-0.1576056	-0.0001656	0.248
5	34	-0.1576467	-0.0000411	0.302
6	50	-0.1576591	-0.0000124	0.323
7	70	-0.1576631	-0.0000040	

least over the region we have carried the work. Just how rapidly this series converges for very large numbers of terms is not known. The single term r_{12} , aside from being the simplest single term of this kind, is in fact the most important term. This one term is, of course, equivalent to an infinite series of $P_l(\cos\theta)$ terms, but it is just the right combination to represent the entire slowly converging series given by our result (13). This term r_{12} not only gives a good account of the angular correlation, but also describes much of the radial correlation as well.

To illustrate this last point we have carried out the variational calculations of $E_2(1)$ and $E_2(0)$ using for each the trial function (11) with a variable coefficient. The surprisingly good result is that in this way we get 99.5% of the s -wave correlation energy and (separately) 94% of the p -wave energy. Keeping this term entire, we find that the choice $\psi_1 = \lambda r_{12} \psi_0$ yields 85% of the total E_2 .

This study was applied to the space-symmetric singlet S state. For other space-symmetric states the numbers would, of course, be different but, we believe, the form of Eq. (13) would still hold; i.e., $E(l) \propto l^{-4}$. For triplet states the wave function has a node at $r_1 = r_2$, where the interaction has its maximum; thus, the strength of the effects we have discussed will be diminished. We would guess that for these states the asymptotic rate of decrease would be l^{-6} .

III. ELECTRON-HYDROGEN SCATTERING

After this first example on the two-electron atom (bound state for large Z), we now turn to our second study: low-energy scattering at $Z=1$. We have recently published⁵ results of variational calculations of singlet and triplet S -wave phase shifts, using trial functions of the form of Eq. (4) with the appropriate asymptotic terms added. Now, considering those results to be exact, we give the results of restricted calculations which admit only $P_0(\cos\theta)$ (relative s waves), and only $P_0(\cos\theta) + P_1(\cos\theta)$ (relative s and p waves) in the trial function. The collected results are shown in Tables II and III. The average errors in the phase shifts, for $0.2 \leq ka_0 \leq 0.8$, are about 0.15 radian (singlet) and 0.04

radian (triplet) for the $l=0$ part alone; and they are reduced to 0.014 and 0.0014, respectively, with the $l=0+l=1$ wave function. The scattering lengths have errors of about 30% for both states using $l=0$ alone; and with $l=0+l=1$ the remaining errors are only 2% (singlet) and 0.7% (triplet). The general summary of these results is the statement that the relative s - and p -wave parts of the wave function account for about 98% of the correct answers in the singlet states, and even more in the triplet states.

TABLE II. Values of $\lambda = (\tan\delta)/ka_0$ for singlet S -state e -H scattering, with various restrictions on the wave function.

ka_0	$\lambda(s)$	$\lambda(s+p)$	$\lambda(\text{complete})$
0.0	-7.815	-6.08	-5.965
0.2	-14.77	-9.60	-9.23
0.4	8.048	14.5	15.87
0.6	2.147	2.76	2.845
0.8	1.110	1.49 \pm 0.02	1.530

IV. DISCUSSION

Any attempt to carry out accurate calculations of the atomic 3-body problem needs first a choice of the basis functions to be used. Hylleraas' choice of r_{12}, r_{12}, r_{12} has led to the most accurate results by far. The chief reason for this success, we believe, is that the term r_{12} represents in just the correct way the major part of the contributions of the states of high relative angular momentum. Alternatively, many people^{6,7} have discussed and attempted to use the expansion in Legendre functions,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{l=0}^{\infty} \Phi_l(r_1, r_2) P_l(\cos\theta). \quad (14)$$

TABLE III. Values of $\lambda = (\tan\delta)/ka_0$ for triplet S -state e -H scattering, with various restrictions on the wave function.

ka_0	$\lambda(s)$	$\lambda(s+p)$	$\lambda(\text{complete})$
0.0	-2.3482	-1.7812	-1.7686
0.2	-2.4908	-2.269	-2.260
0.4	-3.0467	-2.842	-2.833
0.6	-4.8486	-4.41 \pm 0.02	-4.40 \pm 0.01
0.8	-27.24	-17.6 \pm 0.3	-17.2 \pm 0.6

This latter approach is currently very popular among atomic and molecular theorists. It goes under the name of "superposition of configurations" and has the appeal, in its early stages, of providing a more intuitive picture of the complex wave function as built out of a few hydrogenic orbits. But when high accuracy is desired and a large number of terms of (14) are used, this interpretative advantage is lost and the only pertinent

⁶ The first attempt along these lines appears to be the work of P. J. Luke, R. E. Meyerott, and W. W. Clendenin, Phys. Rev. **85**, 401 (1952).

⁷ A recent discussion of several results, along with further references may be found in the paper of J. Linderberg and H. Shull, J. Mol. Spectroscopy **5**, 1 (1960).

⁵ C. Schwartz, Phys. Rev. **124**, 1468 (1961).

question (after one knows how to evaluate all the matrix elements) is how rapidly does this expansion converge?

A number of people⁷ have investigated this question by calculating the ground state of helium with selected terms of (14). The conclusion of nearly all of these works, either explicitly stated, or left implicitly to be drawn from the results given, has been that the expansion in l was rapidly convergent.^{7a} Our claim, in sharp contrast, is that the l expansion converges rather slowly, the contributions to the energy going as l^{-4} for symmetric states and probably as l^{-6} for antisymmetric states.

Now, it may very well be that at low l values the contributions decrease more rapidly and the above asymptotic rates hold only after some rather large (say 5 to 10) l value; or one may decide that these asymptotic rates are not too bad and that it is desirable to carry the work with (14) farther. It then becomes crucial that the function $\Phi_l(r_1, r_2)$ be well represented. For high l values the most important part of this function is concentrated very sharply about the point $r_1=r_2$, and a direct attack on the associated two-dimensional partial differential equations might be the best way to solve for these highly correlated functions. On the other hand, an expansion of $\Phi_l(r_1, r_2)$ in a series of product functions $u_n(r_1)u_m(r_2)$ will be very slowly convergent, and any attempt to use just a few such functions should give wholly inadequate results. Thus, the correct superposition of configurations program will need more and more radial configurations for each added angular component.

We single out for criticism the paper of Tycko, Thomas, and King⁸; this represents the most extensive application of (14) and contains the (erroneous) conclusions typical of the several earlier attempts. In a systematic attack on the helium ground state these authors found rapidly decreasing contributions—about a factor $\frac{1}{3}$ smaller at each step—for all l values added up to $l=8$. However, they used *fewer* radial functions as l increased, and it is our contention that these higher l values are very inadequately represented. This failure should have made itself apparent if an attempt had been made to add more radial functions at any given higher l value in order to test for convergence.

It was noted by the authors that beyond $l=4$ their results were not approaching the correct answer, but were short by 0.00028 a.u. This discrepancy was blamed on an insufficient solution of the leading term, $l=0$, for which they got the upper bound -2.878920 . Shull and Löwdin⁹ reported an upper bound of -2.878970 for this

^{7a} However, conclusions of the more pessimistic kind such as we are here presenting have been drawn already by A. W. Weiss, Phys. Rev. **122**, 1826 (1961). This suggests that other workers in this field are already becoming more critical of the 'superposition of configurations' method. The author thanks J. W. Cooper for calling his attention to the Weiss work.

⁸ D. H. Tycko, L. H. Thomas, and K. M. King, Phys. Rev. **109**, 369 (1958).

⁹ H. Shull and P.-O. Löwdin, J. Chem. Phys. **30**, 617 (1959).

value, termed by them the radial limit, and guessed the correct result was -2.87900 ± 0.00003 . We have extended this restricted calculation (see Appendix) and found the value -2.879028 with an uncertainty of one in the last figure. Thus, the inadequacy of their $l=0$ calculation actually explains only about one-third of the total discrepancy in the work of Tycko *et al.*; the remainder of the discrepancy must be spread out over the many l values, being undoubtedly smaller in absolute magnitude for the higher l terms but, we believe, much larger relative to the correct magnitudes of these contributions.

There are two reservations which should be made concerning the above comparison of our results with previous calculations. First, is the fact that we have studied only the second-order energy while these other studies were concerned with the total energy problem. We have no proof for the parallelism, but we believe that the form of our principle result (13) is probably correct for the complete problem, and we would even put some credence in the numerical coefficient given there, since it is known that the higher terms in (1a) are actually very small even for $Z=2$. Secondly, when other writers (see reference 7) speak of the correlation energy in helium, they mean the difference between the exact energy and the Hartree-Fock approximation. The Hartree-Fock method includes the major part of the radial interaction in an averaged way, and thus what is generally referred to as radial correlation is only a relatively small part of the total wave function. In the high Z limit the Hartree-Fock contribution may be calculated explicitly using a result given previously¹⁰; we find the value^{10a}

$$-E_2(\text{Hartree-Fock}) = (9 \ln \frac{3}{4} - 26/27)/32 = 0.1110032,$$

which checks with the $(ls\ ns) + (ls\ ks)$ parts of the sum (2a) evaluated by Scherr.³ This accounts for 88% of $E_2(0)$ or 70% of the total E_2 ; and thus with this part taken out in the zeroth-order problem the relative importance of all other terms is increased.

On the second problem, e -H scattering, there have also been several attempts at using the basis (14) in a large-scale calculation. Temkin¹¹ has recently obtained results essentially as good as our s wave + p -wave results discussed in Sec. III, although it is not clear how reliable his d -wave contributions are (remember that we are referring to the relative angular-momentum components in the over-all S wave). Also Burke and Schey¹² have reported fairly accurate phase shifts using only s - and p -wave parts with a more restricted choice of radial functions. It thus appears that fairly good results (accurate within a few percent) for the scattering problem are obtainable with these simple wave func-

¹⁰ C. Schwartz, Ann. Phys. (New York) **2**, 156 (1959).

^{10a} J. Linderberg, Phys. Rev. **121**, 816 (1961) has also given this result.

¹¹ A. Temkin, Phys. Rev. **126**, 130 (1962).

¹² P. G. Burke and H. M. Schey, Phys. Rev. **126**, 147 (1962).

tions. But we would again caution against any large-scale program using (14) to get very high accuracy, especially when, as in these other works, $\Phi_l(r_1, r_2)$ is represented in product form.

V. SUMMARY

Our conclusion is that if one needs accuracy only in the range 90% to 98% (roughly speaking), then the Legendre polynomial expansion will give an adequate representation of two- (many?) electron correlated wave functions, using only $l=0$ and $l=1$ terms. But if much greater precision is required, the persistent use of this approach (superposition of configurations) will be both difficult at each step (for higher l values) and rather slowly convergent from one step to the next. Thus, for very accurate representations, the Hylleraas variable r_{12} is essential.

The computations reported here were carried out on the IBM-704 facility of the University of California Computer Center.

APPENDIX

The study of angular correlations leads inevitably to the consideration of radial correlations. In order to check on the radial limit for helium mentioned in the discussion, we attempted a calculation using the standard basis

$$\psi(r_1, r_2) = \sum e^{-2(r_1+r_2)} C_{mn} (r_1^m r_2^n + r_1^n r_2^m). \quad (A1)$$

After we got to about 20 terms (through seventh powers) it became apparent that the convergence was going to be rather slow; and, with growing numerical round-off errors, we could only do slightly poorer than the result of Shull and Löwdin.⁹ We then tried the basis

$$\psi(r_1, r_2) = \sum e^{-2(r_1+r_2)} C_{mn} r_1^m r_2^n, \quad (A2)$$

and found decidedly better convergence, getting the upper bounds -2.8790125 with 21 terms and -2.8790264 with 45 terms.

We would like to suggest that functions of the type $\varphi(r_1, r_2)$ may be generally quite useful. Firstly, these functions (for the two-electron problem) imply no more work in computing matrix elements than the conventional type since the interaction term e^2/r_{12} already necessitates the evaluation of the double (overlap)

integrals. Secondly, and most importantly, these functions are correlated and can very easily represent the type of behavior [as in Eq. (11)] so important for the higher l components and so hard to reproduce by (A1).

It may be thought that these functions are inadmissible as trial functions since they have a (finite) discontinuity in their first derivative at the point $r_1=r_2$. Nevertheless it may readily be seen that the variational principle is still valid, giving an upper bound for the energy. One could easily put constraints on the coefficients in (A2) in order to insure continuity of the first derivatives, or even on all derivatives (this would be incorrect since the potential is not infinitely smooth); but it would be preferable to let the variational principle adjust the coefficients as it wished.

We tried the simplest possible calculation with this correlated function:

$$\psi = e^{-\alpha r_1} e^{-\beta r_2}, \quad (A3)$$

for the helium-ground state; and we got the energy value -2.87274 , which is remarkably good. It surpasses the Hartree-Fock value -2.86168 and lacks only -0.0063 of the radial limit -2.8790 ; or, in another comparison, this leaves only one-fifth of the error (in the angle-independent calculation) of the familiar function $e^{-(Z-5/16)(r_1+r_2)}$. With $Z=1$ a function of the form, (A3) even yielded a bound state for the negative hydrogen ion. This was to our knowledge the first simple wave function to show a bound state, although the value of the ionization energy obtained is very small.

These functions we have been discussing are by construction symmetric in the two coordinates. Antisymmetric states could be represented, for example, by

$$\psi = (r_1 - r_2) \varphi(r_1, r_2). \quad (A4)$$

We attempted the lowest 3S state of helium using $(r_1 - r_2) e^{-\alpha r_1} e^{-\beta r_2}$ and got the energy -2.1608 , which is slightly poorer than the screened hydrogenic result of Eckart¹³: -2.167 . Our failure here is probably due to the poor location of the node in the wave function.

It may be worthwhile investigating whether this correlated type of wave function can be generalized for use in many-electron atoms.

¹³ C. Eckart, Phys. Rev. **36**, 878 (1930).