

ATOMIC PHYSICS

Proceedings of the First International Conference on
Atomic Physics, June 3-7, 1968, New York City

Conference Chairman

VERNON W. HUGHES

Yale University

Editors

BENJAMIN BEDERSON

New York University

VICTOR W. COHEN

Brookhaven National Laboratory

and

FRANCIS M. J. PICHANICK

Yale University

 **PLENUM PRESS • NEW YORK • 1969**

PRECISE SCHRODINGER WAVE FUNCTIONS FOR TWO ELECTRON ATOMS

Charles Schwartz

Department of Physics, University of California,
Berkeley, California

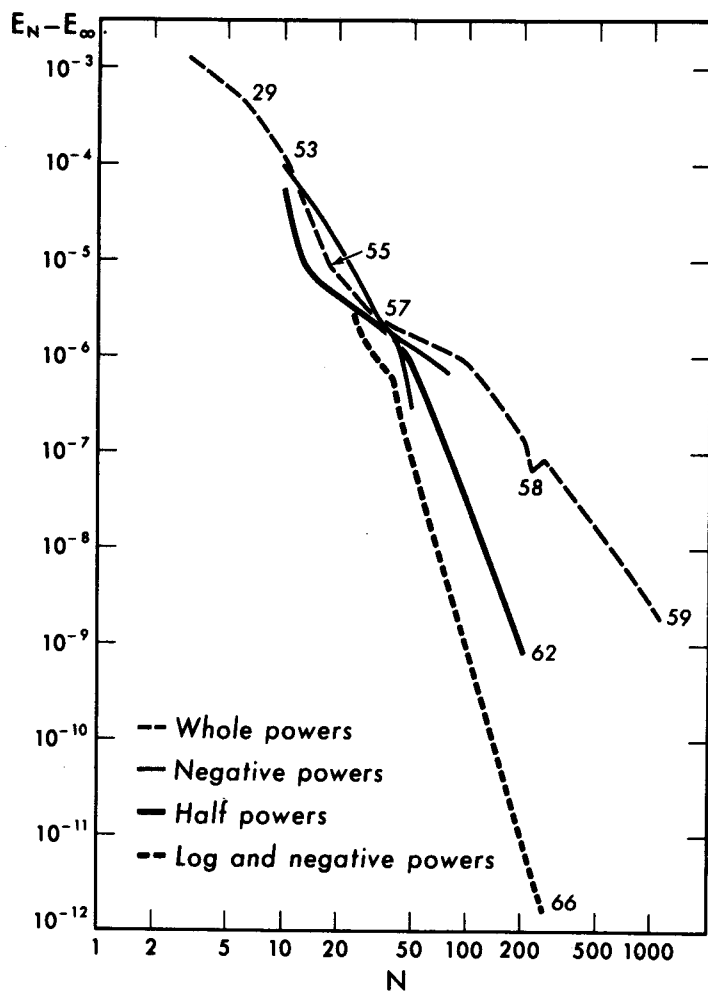
There is the well known statement of some famous physicist at the end of the last century to the effect that fundamental physics was complete, and all that remained was to go on to the next decimal place in this and that calculation. It is the pride of twentieth century physics to put the lie to this prediction; we have relativity and quantum mechanics as our great revolutionary theories, and today, in spite of a certain frustration at the frontiers of our knowledge in particle physics, no one could describe physics as a lifeless subject. Yet in the midst of all the hustle there stands one thread of activity which seems to be following that nineteenth century prediction: for forty years now a persistent clan of physicists have been calculating the wave-function of the helium atom to one more and one more and one more decimal place. Today I am supposed to justify that work.

In spite of the title of this paper I will not present a bunch of twelve digit numbers to impress you, but will just talk about them. Also my talk will not be at all a thorough review of this field, but rather a sketch of the history and an outline of one outstanding current project; so I should begin with a couple of references for those who want to see in detail the wealth of labor that has gone into the study of two-electron atoms. The landmark work is the famous "Quantum Mechanics of One- and Two-Electron Atoms" by Bethe and Salpeter (1957, New York, Academic Press) where the physics is derived and the earlier calculations reported. The more recent review article by A. L. Stewart (Advances in Physics, 12, 299 (1963)) shows the great variety and depth of calculations on these problems which have been undertaken in recent years. The two-electron atom has been an excellent training ground for students

and a testing ground for computationally oriented physicists by providing many hard but tractable problems exercising in perturbation theory, variational or other numerical methods; and these for scattering as well as bound state situations. The sort of effects people have calculated are: eigenvalues for many excited states, relativistic shifts and splittings of levels, Lamb shift, hyperfine structure, finite nuclear mass effects, diamagnetic susceptibility, nuclear magnetic shielding, electric polarizability, nuclear quadrupole shielding, transition oscillator strengths, scattering phase shifts, photoionization cross section; and these not only for helium but for the whole iso-electronic sequence. I will talk here only about two aspects: first the long history of work on the ground state wave function and energy, and second the current work on the fine-structure of the 2^3P state of helium.

The man who started most of this activity is of course E. A. Hylleraas, who in 1929 carried out the first accurate calculation of a complex quantum mechanical system. The spiritual flavor of this long tradition of calculations on helium is best represented by a quotation from Hylleraas' reminiscences on those early days of quantum mechanics (Rev. Mod. Phys. 35, 421 (1963)). After describing how he came to introduce the interelectron coordinate r_{12} into the wave function and thereby achieve excellent agreement between theory and experiment, he goes on to say, "But the tie was loosened and addition of a few more terms ...".

The Figure shows the collected results of the addition of more terms to Hylleraas' calculation of the ground state energy of the non-relativistic helium problem. On a double logarithmic plot we see the decrease in the residual error in the energy E as the number of terms N is increased, as we have better computing machines available, and as we become more sophisticated in our mathematical constructions. Notice that by leaving all names of people off this graph I have hidden one essential feature of this sport: competitiveness. The two digit numbers on the graph indicate the year of each milestone in the advance of precision from 1929 to 1966. The present record is held by Frankowski and Pekeris (Phys. Rev. 146, 46 (1966)). There are many subtleties hidden in this graph which only experts will appreciate, but I will simply say that points in this game are earned by coming out southwest of previous workers: that means getting higher accuracy, using fewer terms, or both. Agreement with experiment was saturated about ten years and five orders of magnitude ago. What one can learn by going on with this work is not directly new physics, but is very useful new experience in numerical analysis. Maybe that sounds disrespectful of the many man-years of labor embodied in this graph, but I believe that numerical analysis is a very important part of physics. The hard problems today, at both low and high energies, are many-body problems, where "many" may mean 3 or 4 or 10^{23} ; and most attempts to



CALCULATIONS OF THE GROUND STATE ENERGY OF THE HELIUM ATOM

solve these problems by using approximation techniques found in the textbooks just do not work. In order to construct approximate wavefunctions in many variables one must choose basis elements which will be very efficient -- even with the largest and fastest computing machines available -- and this means one has to look into the formal analytic properties of the problem in all the dark and hidden corners of a multi-dimensional space. That is hard work, but it is necessary; and I believe that much of the technical advance in these hard problems will be based on experience gained with such exercises as this helium problem.

On the graph are shown four lines of development; they all refer to the form of Hylleraas functions used in the variational calculation:

$$\psi = e^{-s} \sum_s \ell^m u^n t$$

where $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_1 r_2$.

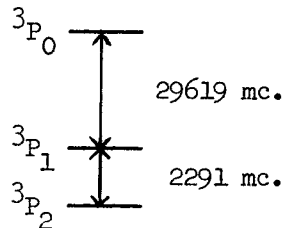
The powers ℓ, m, n were first taken as whole positive integers; later, with various motivations, people have tried negative powers, fractional powers, logarithms, or combinations of these. The analysis of Bartlett and of Fock showed that whole powers alone could not give a formal solution and some complicated logarithmic terms were indicated. The specific introduction of the new forms into the variational calculations was guided more by the "doability" of the integrals involved than by pure analytical requirements, but this is the sort of compromise one learns to expect in this business. However I would note that it was predicted that the slope of the line for half powers would be about twice the slope of the line for whole powers, and that prediction was borne out; and of course we see that the very best results to date have been achieved following the advice of the formal analysis and using logarithm terms. There really is almost as much science as art in this work.

Among the many other problems which have been benefitted by our experience with the Hylleraas problem I would cite two in particular. The study of correlation energies in many electron atoms starts with the isolation of pairwise terms, which brings us back to the two-electron problem in an external field. Also the first accurate calculation of a three-body scattering process in quantum mechanics was work on the elastic scattering of electrons from hydrogen, which used a variational principle with Hylleraas' type of trial function.

Now I shall turn to discussion of the fine-structure in the 2^3P state of helium. I remind you of the energy level scheme:

$$\begin{array}{ll} 2^1S \text{ ---} & 2^3P \text{ ---} \\ & 2^3S \text{ ---} \\ 1^1S \text{ ---} & \end{array}$$

and the details of the $3P$ states:



This problem also has a long and glorious history, for it was here that Breit first showed that application of the new relativistic theory of the electron and the quantised electromagnetic field did give detailed agreement with spectroscopic measurements. The reason for interest in this problem today is that we expect refined measurements and calculations of this energy level splitting to yield the best value of the fine structure constant α . In the previous paper Professor Drell has reviewed the wealth of theoretical and experimental work on one and two particle systems which test the relativistic theory of quantum electrodynamics or QED, and he has shown us that the experiments give us two values for α differing by about one part in 10^5 . This difference is perhaps inside the experimental uncertainties so that one is not sure whether or not there are real interesting discrepancies between theory and experiment. Now it turns out that the lifetime of the 2^3P state in helium is about two orders of magnitude longer than the lifetime of the $2p$ state in hydrogen and so, since the natural linewidth is the dominant source of experimental error, one expects to be able to measure fine structure in helium more accurately than in hydrogen. This is not a new observation: it was ten years ago that one experimentalist and one theorist agreed that it would be possible to get α accurate to one part in 10^6 from an analysis of the helium 2^3P state. The program has not yet been completed because the experiment is fraught with many difficult technical details and the theoretical work required is fraught with many difficult technical details. It has seemed at times as if each party has waited for the other to go first since if either one fails, the labor of the other is wasted. However in the last year there has been a rebirth of enthusiasm and I seriously expect answers before too much longer. Let me now outline the theoretical job.

The zeroth order problem is the non-relativistic hamiltonian for two electrons in the central field of the fixed helium nucleus.

$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}}$$

The next terms in the expansion are the well known fine-structure

terms which come from the Breit interaction and from the reduction of the Dirac one electron operators to non-relativistic forms; these include spin-orbit, spin-spin, spin-other orbit interactions as well as several spin independent terms, for example correction to the kinetic energy. I will denote all these terms as $\alpha^2 H_2$, indicating explicitly their smallness relative to H_0 with powers of the fine-structure constant. Now if we had the solution to the zeroth order problem,

$$H_0 |0\rangle = E_0 |0\rangle$$

then we would write down the perturbation theory expansion for the exact energy as follows.

$$E = E_0 + \alpha^2 \langle 0 | H_2 | 0 \rangle + \alpha^4 \langle 0 | H_2 \frac{1}{E_0 - H_0} H_2 | 0 \rangle \\ + \alpha^4 \langle 0 | H_4 | 0 \rangle + \dots$$

The operator $\alpha^4 H_4$ represents higher order relativistic terms which must be derived by some super-Breit theorist; I will talk more about this shortly. The three main jobs are indicated in this formula.

I. The zeroth order wave function is of course not known exactly. What we do is construct successive approximations, a la Hylleraas, with more and more terms and see how the resulting approximations to $\langle 0 | H_2 | 0 \rangle$ converge. Since this is the leading term in the fine-structure we need this expectation value accurate to one part in 10^6 , which is our goal for α . This is not a trivial job since to get the wave function accurate to 10^{-6} one has to get the energy accurate to almost the square of this number, and so this job is at the frontier of the work represented in the Figure. However by brute force this calculation has been successfully completed; whether the final accuracy is really one part in 10^6 or two or three parts may be open to question, but if need be one could carry the program another step or two forward and settle the matter.

II. The second order perturbation expression

$$\langle 0 | H_2 \frac{1}{E_0 - H_0} H_2 | 0 \rangle$$

is indeed a formidable looking thing to evaluate. Fortunately since this is a correction to the leading fine-structure term of relative order α^2 , or about 10^{-4} , we have to evaluate this to only about one percent accuracy. The usual formula in matrix mechanics expresses this second order energy as a sum over all intermediate states with matrix elements and energy denominators. I think a more tractable method is the one that sets out to solve inhomogeneous Schrodinger equations. If we write the equation

$$(E_0 - H_0)\psi_1 = H_2\psi_0,$$

then we see that the single integral

$$\int \psi_0^* H_2 \psi_1$$

gives us directly the desired answer. The work of course lies in solving the equation for ψ_1 , but this can be formulated as a variational principle and so it gets to look just like another Hylleraas type calculation. I presently have a graduate student working on this and of course he finds some important details of the problem which make it more tricky than the original Hylleraas problem. One thing is that the angular part of the function ψ_1 has not only P-state parts but D-state and F-state parts as well. A more serious consideration is the fact that the operators in H_2 are rather singular at small distances (spin-orbit forces generally behave as $1/r^3$); and so the function ψ_1 must be properly constructed to respond to this singularity, and this can make a lot more work in terms of the integrals one has to evaluate. A great deal of algebra and a great deal of computer programming will be needed to complete this phase of the work, but now that it has begun in earnest I can begin to anticipate its completion.

III. The third, and to me most complex job is the derivation of the higher order terms H_4 and the computation of their expectation values. Here again only about one percent accuracy is required so relatively simple helium wavefunctions should suffice; but the work of starting from the complete relativistic field theory and deducing all the terms of this small order is really a challenge. The most advanced QED work that has been done in the hydrogen atom is at the same order as that we require, and our atom has two electrons to deal with instead of one. In fact a complete energy level calculation for helium to the order we need may be completely out of the question, but what makes our job only difficult rather than impossible is the fact that we are looking only at the fine-structure splitting and thus all spin independent effects can be ignored.

To get an idea of the many complicated radiative corrections that we expect to ignore I suggest you look at any recent article on the complete Lamb shift calculation, and then look at the very simple formula for the fine-structure splitting in hydrogen:

$$\begin{aligned} & \Delta E(2p_{3/2} - 2p_{1/2}) \\ &= \frac{\alpha^2 R_y}{16} \left[1 + \frac{5}{8} \alpha^2 + 2 \left(\frac{\alpha}{2\pi} - .328 \frac{\alpha^2}{\pi} \right) + \frac{2}{\pi} \alpha^3 \ln \alpha \right] \end{aligned}$$

This is not only a short formula, but an understandable one. The first correction term ($5/8 \alpha^2$) comes from expanding the solution of the one electron Dirac equation and thus it is not concerned with radiative effects at all. The two terms in parenthesis are just the anomalous magnetic moment of the free electron. (The factor of two comes in because the Thomas factor in spin-orbit coupling applies to the Dirac magnetic moment but not to the Pauli type anomalous moment.) The last term, first calculated by A. Layzer (J. Math. Phys. 2, 308 (1961)), is a real radiative correction to the spin interaction in the bound state. For our requirements on accuracy we may either ignore this term, or perhaps expect to be able to adapt the result from hydrogen simply to the helium atom.

A first attack on the big problem of these higher order relativistic corrections for helium was made a few years ago by a student of mine, K. Y. Kim (Phys. Rev. 140, A1498 (1965)). He wrote down a sum of two Dirac hamiltonians for the two electrons, added the interaction with the quantised transverse electromagnetic field along with the Coulomb interaction. Then proceeding systematically to expand in powers of α he got H_0 , H_2 and finally a very big formula for H_4 . This procedure is known not to be really the right way to start, and it was necessary to cheat a bit in order to get the anomalous magnetic moment and to ignore many divergent (but spin independent) terms. But at least this was a start on the work; and I would not be overly surprised if it turns out that the final result Kim got for H_4 is actually correct. I now have another graduate student starting to work at evaluating the expectation values of these H_4 operators with a modest helium wave function.

The newest and best news is a recent private communication I have from a student of Professor Kroll, Marvin Douglas is his name, and he is doing the correct relativistic analysis of the helium fine-structure problem. He starts with a Bethe-Salpeter equation, isolates the Coulomb potential, separates positive energy parts, and then expands everything else in a perturbation sense. This work is not yet complete; but as far as it has progressed there seem to be no surprises, and it appears that the final results will be known soon. I believe even the $\log \alpha$ term will be included in Douglas' results.

There are a few non-QED effects one will have to consider due to the nucleus having finite mass, size and polarizability. These have not been studied completely but I expect they will offer no difficulties.

To summarize: this problem of measuring and calculating the helium fine-structure to an accuracy of about one part in 10^6 is very important and it is very hard. I believe now, as I did ten years ago, that it is manageable. The recent activity convinces

me that the calculations will be completed soon, but I would not dare promise that the final answer will be available a year from now. So if it is planned to make an annual affair of this International Conference on Atomic Physics, you may well find that the first 41 years of work on the helium atom is not noticeably different from the first 40 years.