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Perspective

Perspective on "Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium"

Hylleraas EA (1929) Z Phys 54: 347–366

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Abstract. Hylleraas' paper on the ground state of the helium atom represents the first ab initio calculation on a two-electron system in quantitative agreement with experiment. As such, it served not only as an important numerical verification of wave mechanics, it also exposed the shortcomings of determinantal expansions for accurate calculations of molecular and atomic electronic structure. By the simple addition of terms linear in the interelectronic distance, dramatic improvements in the description of the electronic wave function were achieved. The generalization to larger systems of chemical interest has proven difficult but interest in the techniques pioneered by Hylleraas has grown in recent years, prompted by progress in computer technology.

Key words: Helium atom – Electron correlation – Explicitly correlated wave functions – Hylleraas expansion

When Egil Andersen Hylleraas came to Göttingen to work with Max Born in 1926, he arrived with a background in crystallography and began work on the optical properties of quartz crystals. However, this was in the early days of wave mechanics and Born was more eager to work on the helium atom. The one-electron hydrogen atom had, of course, been worked out by then, but the study of many-electron atoms had barely begun. Heisenberg [1] had formulated the helium problem quantum mechanically in 1926, but a simple first-order perturbational treatment by Unsöld [2] had yielded an ionization potential of only 20.41 eV[1]. Compared with the experimental measurement of 24.59 eV, this was not better than the numerical value of 28.29 eV, which followed from the earlier Bohr theory. Born, therefore, considered it crucial to have a much better agreement with experiment to confirm the correctness of wave mechanics.

Born already had a student working on this problem, but this student fell sick and Hylleraas was given the task to carry on the urgent work. Hylleraas modified the original attempt in two ways. First, in the expansion of the wave function, he replaced the incomplete set of the bound-state hydrogenic functions by the complete set of Laguerre functions. Second, he simplified the treatment of the ground state by reducing the number of coordinates from 6 to 3: the distances r_1 and r_2 of the two electrons from the nucleus and the angle θ between the two position vectors of the electrons. Then, taking advantage of a newly installed desk calculator, he obtained an ionization potential of 24.47 eV [3] – merely 0.12 eV below the experimental number.

In the meantime, while Hylleraas was carrying out his work, other papers on the same problem appeared during 1927. By essentially the same variational method – today known as the configuration-interaction (CI) method – Kellner [4] in Berlin calculated the ionization potential of helium but obtained a result less conclusive than that of Hylleraas since a shorter expansion was used. Furthermore, using a different, nonvariational method, Slater [5] in Cambridge, Massachusetts and Sugiura [6] in Copenhagen both obtained good agreement with experiment – in fact, as good as Hylleraas. So, by 1928, several independent calculations on the helium atom appeared to have confirmed the validity of wave mechanics.

Still, there was a discrepancy of 0.12 eV that continued to bother Hylleraas when he returned to Oslo in 1928. Hylleraas considered this discrepancy a serious problem. On the one hand, attaching great importance to the variational principle, he was happy to see that his calculations approached the experimental number from the right side. On the other hand, he could not see how further extensions of the CI expansion could improve the situation much, hinting at a limit of 24.49 eV [3] – still

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[1] The unit of 1 eV in the old literature is different from today's value (used in this article), the relationship being 1 eV (old) = 1.005 eV (new).

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0.10 eV below the experimental value. Nevertheless, he stated cautiously that it would be premature to conclude that wave mechanics is in some manner deficient [3]. Rather, he kept on trying to improve the helium wave function.

Later in 1928, a breakthrough was reached when he noted a peculiarity of the CI wave function. Expressing $\cos\theta$ in terms of r_1, r_2, and r_{12}, he realized that the wave function contains arbitrary powers of r_1 and r_2 but only even powers of r_{12}. This seemed to him unsatisfactory since the radial Hamiltonian treats these three variables in a more symmetrical fashion. He therefore decided to treat the three variables on the same footing, adding to the CI expansion terms of odd powers in r_{12}. With this inclusion, everything fell into place; to Hylleraas himself, it had almost the effect of a miracle. Thus, with only three terms in the first *Hylleraas expansion*, he obtained 24.56 eV; with six terms, he obtained 24.58 eV. The error had been reduced to 0.01 eV – i.e. to the same order of magnitude as the corrections arising from relativity and nuclear motion. Hylleraas was aware of these corrections and their approximate magnitudes and concluded that there were no remaining discrepancies between wave mechanics and experiment for the helium atom. His results were published in *Zeitschrift für Physik* in early 1929 under the title "Neue Berechnung der Energie des Heliums im Grundzustande, sowie des tiefsten Terms von Ortho-Helium" [7]. As the title indicates, he also considered the singlet–triplet splitting of the helium atom, which he reproduced to within 0.01 eV of the experimental number.

Hylleraas was thus not only the first person to experience the slow convergence of the CI expansion. He also solved the problem – at least for the two-electron system. However, Hylleraas had not arrived at his wave function from a consideration of the singularities of the Hamiltonian. In fact, in 1928, Slater had analyzed the properties of the helium wave function and had found that the Coulomb singularity in the Hamiltonian imposes a certain behaviour on the wave function when the electrons coincide and had suggested that the wave function be multiplied by a factor of $\exp(r_{12}/2)$ in order to model this behaviour [8]; however, less interested in numerical solutions and applied mathematics than Hylleraas, he did not attempt to include this factor in the wave function to resolve the discrepancy with experiment for helium. In retrospect, therefore, it appears that the explicitly correlated techniques of quantum chemistry were pioneered by both Hylleraas and Slater.

Hylleraas' work on helium was quickly applied to other two-electron atoms and in 1933 generalized to diatoms by James and Coolidge [9], who were able to compute the energy of the hydrogen molecule with an error of less than 0.03 eV. Clearly, Hylleraas' method had the potential for high accuracy for molecules as well. Nevertheless, the immediate practical impact of Hylleraas' work on chemistry was limited since it appeared difficult if not impractical to apply his ansatz to polyatomic systems. For many years, the most fruitful nonempirical approach to the many-electron problem in chemistry was firmly based on the ideas of orbitals and determinants. Certainly, the determinantal approach has been a highly successful one and still continues to be the workhorse of computational chemistry; however, with the steady improvements in computational techniques and computer technology, the slow convergence of the determinantal expansion, first realized by Hylleraas for the helium atom, has come back to frustrate progress towards highly accurate solutions for chemical systems. Like Hylleraas for the helium atom, chemists must now find a way to solve this problem by including in their ansatz for the wave function some explicit dependence on the interelectronic distance.

Acknowledgement. In preparing this article, we made use of Hylleraas' own recollections "Reminiscences from early quantum mechanics for two-electron atoms" [10].

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