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ABSTRACT

This article explores the place of computation in the history of quantum theory by examining the development of several approximation methods to solve the Schrödinger equation without using empirical information, as these were worked out in the years from 1927 to 1933. These *ab initio* methods, as they became known, produced the results that helped validate the use of quantum mechanics in many-body atomic and molecular systems, but carrying out the computations became increasingly laborious and difficult as better agreement between theory and experiment was pursued and more complex systems were tackled. I argue that computational work in the early years of quantum chemistry shows an emerging practice of theory that required human labor, technological improvement (computers), and mathematical ingenuity.

KEY WORDS: computation, computer, quantum chemistry, practice of theory, approximation method, *ab initio,* Douglas Hartree, John Slater, Walter Heitler, Hubert James

INTRODUCTION

In the traditional narrative of the history of quantum physics, the problem of chemical binding appears only briefly at the end of the long march toward quantum mechanics. It is usually introduced as one of the exemplary problems

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The following abbreviations are used: *AHC*, *Annals of the History of Computing; HSPS, Historical Studies in the Physical and Biological Sciences; JCP*, *Journal of Chemical Physics;* JSP, John C. Slater Papers, American Philosophical Society, Philadelphia; PCPS, Proceedings of the Cambridge Philosophical Society; *PR*, *Physical Review;* PRS, Proceedings of the Royal Society; *RMP*, *Reviews of Modern Physics;* SCF, self-consistent field; *SHPMP*, *Studies in History and Philosophy of Modern Physics; ZP, Zeitschrift für Physik*.

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that quantum mechanics solved, thereby validating its general applicability. Singularly recognized as groundbreaking is Walter Heitler and Fritz London's famous paper of 1927, which provided a theoretical explanation of why two hydrogen atoms combine to form a molecule.[1] The possibility of understanding the whole territory of chemistry with quantum mechanics—a reductionist ideal shared by other physicists—seemed within Heitler and London's reach.[2] Indeed, excitement about the new theoretical framework abounded in the late 1920s. As the historian Max Jammer put it: "Satisfied that the theory 'works,' since it provided unambiguous answers whenever invoked, physicists engaged themselves rather in solving problems which so far had defied all previous attempts or which promised to open up new avenues of research."[3]

However, historians of quantum physics, including Jammer, have paid little attention to whether the reductionist program worked well or faced difficulties in chemistry after 1927. It seems that they have largely believed that quantum chemistry, a new field which came into being after Heitler and London's paper, successfully carried out the mission of reducing chemistry to physics. Historians of quantum chemistry have been rather critical of this picture. They have shown that early optimism about reductionism quickly devolved into pessimism in the 1930s in the face of the complexity of chemical systems, and that quantum chemistry developed into a discipline with diverse methodologies, indigenous languages, and separate institutional bases. To them, the acceptance of quantum mechanics in chemistry has not necessarily meant the reduction of one discipline to another.[4]

1. Walter Heitler and Fritz London, "Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik," *ZP* 44 (1927): 455–72.

2. For instance, Paul Dirac made an oft-quoted statement that "the underlying physical laws for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known." P. A. M. Dirac, "Quantum Mechanics of Many-Electron Systems," *PRS* A123 (1929): 714–33, on 714.

3. Max Jammer, *The Conceptual Development of Quantum Mechanics,* 2nd ed. (College Park, MD: American Institute of Physics, 1989), 359–60, 384–86.

4. Kostas Gavroglu and Ana I. Simões, "The Americans, the Germans, and the Beginnings of Quantum Chemistry: The Confluence of Diverging Traditions," *HSPS* 25, no. 1 (1994): 47–110; Eric R. Scerri, "Has Chemistry at Least Been Approximately Reduced to Quantum Mechanics?" *Proceedings of the Biennial Meeting of the Philosophy of Science Association* 1 (1994): 160–70; Mary Jo Nye, *From Chemical Philosophy to Theoretical Chemistry* (Berkeley: University of California Press, 1993); Silvan S. Schweber, "The Young John Clarke Slater and the Development of Quantum Chemistry," *HSPS* 20, no. 2 (1990): 339–406. See also Ana I. Simões, "Chemical Physics and Quantum Chemistry in the Twentieth Century," in *The Cambridge History of Science, Vol. 5: The Modern Physical and Mathematical Sciences,* ed. Mary Jo Nye (Cambridge: University of Cambridge

While agreeing in general with the latter point of view,[5] I would point out that most historians of quantum chemistry have not fully examined the efforts made following Heitler and London to solve the Schrödinger equation for multi-electron atomic or molecular systems without using empirical data.[6] This paper thus aims to reassess the place of the pioneers of *ab initio* methods in the history of quantum theory. I suggest that we broaden our attention from the *conceptual* development of quantum mechanics to the *practice* of theory in order to appreciate the significance of computation-oriented work in the spread of quantum mechanics into various problems in physics and chemistry. By the "practice of theory" I mean, in this case, a set of activities required to solve the Schrödinger equation, such as devising approximate Hamiltonians and trial functions, calculating complicated integrals, and formulating schemes to narrow the gap between theory and experiment. There was no dearth of problems to solve. And yet, the more complex the atomic or molecular system, the more difficult the problem, especially because of the increasing amount of labor that computations involved. A compromise had to be reached between defining a manageable problem and solving it accurately. What, then, would be this acceptable compromise? By shifting our focus to the practice of theory, we can see who sought to solve the wave equation using *ab initio* approaches and how they tested the level of compromise between manageability and accuracy. It is worth noting that graduate students, postdoctoral scholars, and junior faculty members created this domain of study, not the inventors of quantum mechanics. That is, the multi-electron atomic or molecular system presented itself as an

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Press, 2003), 394–412; Ana I. Simões, "Dirac's Claim and the Chemists," *Physics in Perspective* 4 (2002): 253–66. Most recently, see Martha L. Harris, "Chemical Reductionism Revisited: Lewis, Pauling, and the Physico-Chemical Nature of the Chemical Bond," *Studies in History and Philosophy of Science* 39 (2008): 78–90.

5. Buhm Soon Park, "In the 'Context of Pedagogy': Teaching Strategy and Theory Change in Quantum Chemistry," in *Pedagogy and the Practice of Science: Historical and Contemporary Perspectives,* ed. David Kaiser (Cambridge, MA: MIT Press, 2005), 287–319; Buhm Soon Park, "Chemical Translators: Pauling, Wheland, and Their Strategies for Teaching the Theory of Resonance," *British Journal for the History of Science* 32 (1999): 21–46.

6. One notable exception is Andrea Woody, "Putting Quantum Mechanics to Work in Chemistry: The Power of Diagrammatic Representation," *Philosophy of Science, Proceedings* 67 (2000), S612–S627. And yet, Woody gives much attention to the emergence of diagrammatic representation of molecular orbitals as a way of getting around computational difficulties. I focus more on the nature of computational constraints and some developments in approximation methods during this period. The term *ab initio*, which means "from the beginning," was first used around 1950. Peter W. Atkins, *Quanta: A Handbook of Concepts,* 2nd ed. (Oxford: Oxford University Press, 1991), 1.

entry-level problem for those who aspired to learn and master quantum theory, although they were located at various universities around the world.[7]

MAKING APPROXIMATIONS

The point of departure for the problem of many-electron atoms was the normal helium atom—the two-electron system. Various approximation methods were first developed and tested for the helium atom before being applied to larger atoms, and that experience would prove important for quantum chemistry in its wake. Outstanding agreement between theory and experiment for the helium problem was achieved by the Norwegian physicist Egil A. Hylleraas. Hylleraas received his PhD from the University of Oslo in 1924, working on crystal lattice theory. After two years as a schoolteacher, he joined Max Born's group in Göttingen on a fellowship from the International Education Board in the hope of furthering his work on crystals. But, following Born's suggestion, Hylleraas decided to study problems related to the application of quantum mechanics.[8]

At that time, a basic understanding of the spectral properties of helium had been well established by Werner Heisenberg—but there was still a broad gap between spectroscopic measurements of the ionization energy (24.46 eV) and its numerical calculation, either by the old quantum theory (28 eV) or by a simple perturbation treatment of the Schrödinger equation (20 eV).[9] The introduction of the effective nuclear charge by the German physicist Georg W. Kellner reduced the discrepancy in the new quantum-mechanical treatment from about 4 to 1.5 eV, which was still, however, a significant amount.[10]

7. A growing body of literature examines the practice of theory. Of particular relevance, for their emphasis on calculations and their pedagogical implications, are David Kaiser, *Drawing Theories Apart: The Dispersion of Feynman Diagrams in Postwar Physics* (Chicago: University of Chicago Press, 2005), and Andrew Warwick, *Masters of Theory: Cambridge and the Rise of Mathematical Physics* (Chicago: University of Chicago Press, 2003). See also Jed Z. Buchwald, *Scientific Practice* (Chicago: University of Chicago Press, 1995), for a general discussion of "practice" in science, including experiments.

8. For Hylleraas's educational background and Born's influence, see Egil A. Hylleraas, "Reminiscences from Early Quantum Mechanics of Two-Electron Atoms," *RMP* 35 (1963): 421–31.

9. Albrecht Unsöld, "Beiträge zur Quantenmechanik der Atome," *Annalen der Physik* 82 (1927): 355–93.

10. Georg W. Kellner, "Die Ionisierungsspannung des Heliums nach der Schrödingerschen Theorie," *ZP* 44 (1927): 91–112.

The effective nuclear charge took into consideration the screening effect of electrons around the nuclei—the effect that the electronic orbits are contracted into a smaller region because of the Coulomb attraction between electrons and nuclei. Under Born's guidance, Hylleraas began to attack the problem using a noisy electric desk calculator called the Mercedes Euclid in order to handle the large volume of numerical work. Using a trial wave function that might be interpreted as representing one electron in an inner orbit and the other in an outer orbit, Hylleraas obtained a good result, 24.35 eV.[11] That 1928 result was soon "greatly admired and thought of as almost a proof of the validity of wave mechanics, also, in the strict numerical sense."[12] Not fully satisfied, however, Hylleraas continued to work on reducing the discrepancy after returning to Oslo. Finally, he made a major advance by introducing into the wave function a new coordinate for the interelectronic distance, $u = r_{12}/a_0$, which occurred in the interaction term for the two electrons (a_0 is the Bohr radius, the mean distance of an electron from the nucleus in the ground-state hydrogen atom). The final theoretical value for the energy of the helium atom was only 0.0016 eV below the experimental value. A discrepancy of this sort could be attributed to a numerical error in the calculations, to experimental error, or possibly to some small effects such as electron-spin interactions, nuclear motion, and so on.[13] This was seen as a triumph for quantum mechanics as applied to many-electron atoms—as Linus Pauling and E. Bright Wilson put it, the "success of this program would strengthen our confidence in our wave-mechanical equations, and permit us to proceed to the discussion of many-electron atoms and molecules."[14]

And yet it was not easy to adapt Hylleraas's method to heavy atoms, as the number of terms that had to be computed increased very rapidly with the number of electrons. The reason was the appearance of the interelectronic coordinate. Even in the early 1960s, no successful application of the method was reported for atoms heavier than lithium, a three-electron system.[15] Hylleraas also

11. Egil A. Hylleraas, "Über den Grundzustand des Heliumatoms," *ZP* 48 (1928): 469–94.

12. Hylleraas, "Reminiscences" (ref. 8), 427.

13. Egil A. Hylleraas, "Neue Berechnung der Energie des Heliums in Grundzustande, sowie des tiesfsten Terms von Orthohelium," *ZP* 54 (1929): 347–66; Egil A. Hylleraas, "Über den Grundterm der Zweielektronenprobleme von H^-, He, Li^+, Be^{++} usw.," *ZP* 65 (1930): 209–25; Linus Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics with Applications to Chemistry* (New York: McGraw-Hill, 1935), 224.

14. Pauling and Wilson, *Introduction* (ref. 13), 222–24.

15. John C. Slater, "The Electronic Structure of Atoms—The Hartree-Fock Method and Correlation," *RMP* 35 (1963): 484–87.

developed an alternative approach, the configuration interaction method, to deal with the interelectronic interaction. Instead of approximating the true wave function with one-electron functions, he devised a way to use a basic set of functions of any number, possibly an infinite number.[16] But he could not apply this method to complex systems either, because of mounting computational difficulties.

Using wave functions of simple analytic form would have been less accurate than Hylleraas's two methods, but more easily applied. The hydrogen eigenfunctions—the solutions of the Schrödinger equation for the hydrogen atom—were such functions; in fact, they were exact solutions for other atomic problems when the interaction between the electrons was entirely neglected. Kellner had partly taken care of the latter interaction in helium by putting in an effective nuclear charge and fixing its value with the mathematical technique known as the Ritz method or the variational principle, determining the coefficients of the linear combination of hydrogen eigenfunctions in a way that gave the lowest energy. This technique was soon applied to lithium and the other elements in the first row of the periodic table, using their asymptotic form (a form at the large distance between nucleus and electrons) instead of the original wave functions of hydrogen. The modified wave functions had the same angular part as their hydrogen counterparts had, but their radial part, $r^{n^*-1}e^{-[(Z-s)r/n^*]}$, was different in that it had no radial nodes.[17] (Here r is the distance between nucleus and electron, n^* the effective quantum number standing in for the principal quantum number, Z the nuclear charge, and s the screening constant.) In 1930 the American physicist John C. Slater used this form of wave function to discuss the size, ionization potential, and magnetic properties of much heavier atoms such as iron and cobalt—hence the name Slater-type orbitals (STOs). Yet Slater did not determine the screening constants and other parameters by the variational principle, but adjusted them using empirical values. Slater's approach here was semi-empirical, as he noted: "It is to be hoped that eventually a variation calculation can be made here too; but we may anticipate that the figures given in this paper will be substantially verified, and in the meantime, an approximate set of functions is much better than none."[18]

16. Hylleraas, "Heliumatoms" (ref. 11).

17. Victor Guillemin, Jr. and Clarence Zener, "Über eine einfache Eigenfunktion für den Grundzustand des Li-atoms und der Ionen mit drei Elektronen," *ZP* 61 (1930): 199–205; Clarence Zener, "Analytic Atomic Wave Functions," *PR* 36 (1930): 51–56.

18. John C. Slater, "Atomic Shielding Constants," *PR* 36 (1930): 57–64, on 57.

THE COMPUTATIONAL TURN IN QUANTUM CHEMISTRY

As for molecular problems, in 1927 the two German physicists Walter H. Heitler and Fritz London published their landmark paper treating the hydrogen molecule with quantum mechanics and studying the source of its binding energy. In view of the significance of this paper in quantum chemistry, it is interesting to note that the encounter of Heitler and London was incidental, and their collaboration short-lived. Both Heitler and London were products of the University of Munich, trained in different areas: London received his PhD in philosophy in 1921 and spent some years in a teaching job before he decided to study theoretical physics under Sommerfeld; Heitler worked on the theory of concentrated solutions for his doctoral degree, which he received in 1925, and went to Copenhagen to continue his work on physical chemistry with Niels Bjerrum. Their paths converged in 1927 when both received Rockefeller Fellowships and went to Zurich to learn wave mechanics under Schrödinger. After publishing their joint paper, Heitler and London continued to study the problem of the chemical bond for some years, but subsequently their interests diverged, Heitler moving into quantum field theory and London into superconductivity.[19]

Heitler and London's basic idea was to regard the molecule as composed of atoms, a view not unlike the traditional conception of the molecule in chemistry.[20] But Heitler and London adopted it as part of applying the approximation technique known as perturbation theory, which had been developed in celestial mechanics and used in the old quantum theory. Assuming that the atoms were set apart at infinite internuclear distance, they first approximated the spatial wave function (Ψ) of the hydrogen molecule with products of the known eigenfunctions of the hydrogen atom, ψ_1 and φ_2, where ψ_1 was the eigenfunction of electron *1* at nucleus *a* and φ_2 was that of electron *2* at nucleus *b*. At this point, the interaction between the atoms could be neglected. However, as the atoms came closer together, the interatomic interaction could no longer be ignored. Heitler and London treated this interaction among two electrons and two nuclei as the perturbation of the system.

19. Nevill F. Mott, "Walter Heinrich Heitler," *Biographical Memoirs of the Fellows of the Royal Society* 28 (1982): 141–51, and Kostas Gavroglu, *Fritz London: A Scientific Biography* (Cambridge: Cambridge University Press, 1995).

20. For reactions to Heitler and London's paper, see Gavroglu, *Fritz London* (ref. 19), 51–53; Gavroglu and Simões, "The Americans, the Germans" (ref. 4), 70–75.

Here Heitler and London found that the perturbation included not only the usual Coulombic interaction between electrons but also a possibility of electron exchange (*Austausch*). Because the electrons were indistinguishable, it was also necessary to consider the case in which electron *1* might be near nucleus *b* and electron *2* near nucleus *a*. Therefore, $\varphi_1\psi_2$ being as acceptable an approximation of Ψ as $\psi_1\varphi_2$, the correct representation would be linear combinations of $\psi_1\varphi_2$ and $\varphi_1\psi_2$:

$$\Psi_\alpha = \frac{1}{\sqrt{2+2S}}\,(\psi_1\,\varphi_2 + \psi_2\,\varphi_1)$$
$$\Psi_\beta = \frac{1}{\sqrt{2-2S}}\,(\psi_1\,\varphi_2 - \psi_2\,\varphi_1)$$

where S (the overlap integral) was given by $\int \psi_1\varphi_1\psi_2\varphi_2 d\tau$. Putting these values into the Schrödinger equation, with R denoting the internuclear distance, r_{12} the distance between the two electrons, r_{a1} the distance between the nucleus *a* and the electron *1*, and so on, they obtained two different energy levels, E_α and E_β:

$$E_\alpha = E_{11} - \frac{E_{11}S - E_{12}}{1+S} = \frac{E_{11} + E_{12}}{1+S}$$
$$E_\beta = E_{11} + \frac{E_{11}S - E_{12}}{1-S} = \frac{E_{11} - E_{12}}{1-S}$$

where E_{11} and E_{12} were integrals of the following form:

$$E_{11} = \int\left[\left(\frac{e^2}{r_{12}} + \frac{e^2}{R}\right)\frac{\psi_1^{\,2}\varphi_2^{\,2} + \psi_2^{\,2}\varphi_1^{\,2}}{2} - \left(\frac{e^2}{r_{a1}} + \frac{e^2}{r_{b2}}\right)\frac{\psi_2^{\,2}\varphi_1^{\,2}}{2} - \left(\frac{e^2}{r_{a2}} + \frac{e^2}{r_{b1}}\right)\frac{\psi_1^{\,2}\varphi_2^{\,2}}{2}\right] d\tau$$

$$E_{12} = \int\left(\frac{2e^2}{r_{12}} + \frac{2e^2}{R} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}\right)\frac{\psi_1\varphi_2\psi_2\varphi_1}{2}\, d\tau.$$

After obtaining this mathematical expression for the energy of H_2, Heitler and London considered the physical meaning of E_α and E_β and their components, E_{11} and E_{12}. It was certain that E_{11} had to do with the "Coulombic

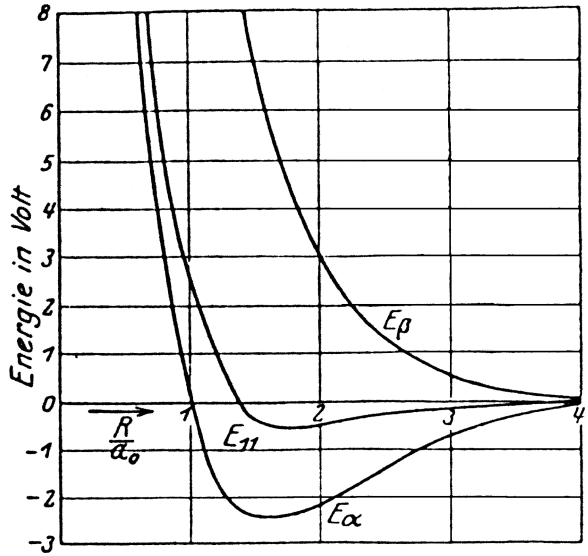

FIG. 1 Heitler and London's energy diagram of the hydrogen molecule. E_α represents nonpolar attraction; E_β elastic reflection; and E_{11} Coulomb interaction. *Source:* Heitler and London, "Wechselwirkung neutraler Atome" (ref. 1), 462. With kind permission of Springer Science + Business Media.

interaction of the present charge distribution,"[21] and that this integral could be solved analytically as a function of the internuclear distance R. By contrast, E_{12} did not permit such a simple, classical interpretation. Moreover, it was difficult to calculate all the integrals involved in E_{12}, particularly the one known as the exchange integral, $\int \psi_1\varphi_2\psi_2\varphi_1/r_{12}\, d\tau$. Heitler and London circumvented this difficulty by considering only its upper limit and drew approximate graphs of E_α and E_β. According to this energy diagram, E_β represented a repulsion between the atoms at any internuclear distance, while E_α showed attraction at larger distances and repulsion at smaller ones, obtaining its minimum value when the internuclear distance R was $1.5a_0$ (or 0.8Å). From the graph of E_α, the corresponding dissociation energy or the binding energy was about 2.4 eV.[22]

21. Heitler and London, "Wechselwirkung neutraler Atome" (ref. 1), 461.

22. Gavroglu and Simões have mistakenly said that Heitler and London obtained 72.3 kcals (about 3.2 eV) for the binding energy of the hydrogen molecule. Gavroglu and Simões, "The Americans, the Germans" (ref. 4), 63, and Gavroglu, *Fritz London* (ref. 19), 47. As I will show, this value was in fact obtained by Yoshikatsu Sugiura, who computed the exchange integral which Heitler and London had roughly estimated.

Heitler and London did not compare their theoretical values with observed ones, presumably because the agreement for the binding energy was not particularly good. But they seemed to place less emphasis on the quantitative argument than on the interpretative promise of their treatment, which explained the attraction between the two nonpolar hydrogen atoms without considering perturbation by polarization. This was due to electron exchange, a "characteristic quantum-mechanical effect." Represented by the integral E_{12}, the exchange effect affected E_β as the van der Waals repulsion ("elastic reflection") of two hydrogen atoms; and it contributed to E_α as the strength of the molecular binding (i.e., the chemical bond).[23]

What was the nature of this exchange effect? Why did nonpolar hydrogen atoms interact in two different ways, attraction and repulsion? Heitler and London could conveniently define the frequency of exchange by the energy difference of E_α and E_β divided by the Planck constant, $(E_\beta - E_\alpha)/h$. But they found it difficult to characterize this effect in terms of classical mechanics. They were at least able to describe the exchange effect as "closely related with the quantum mechanical resonance phenomenon" introduced by Heisenberg a year earlier for the helium problem, in that both resonance and exchange originated from the indistinguishability of electrons.[24] Yet Heitler and London noted some subtle differences: "While, in resonance, electrons of different energy levels in the same set of eigenfunctions exchange their energy, here, electrons of the same state (the same energy) yet different eigenfunction systems (ψ and φ) exchange their places."[25]

The interpretation of E_α and E_β was important in another way. According to the Pauli exclusion principle, the total wave function (in this case, ψ_α or ψ_β times the spin wave function) should be antisymmetric. This requires E_α to be an energy state in which the electrons are in opposite spin orientations (antiparallel), i.e., the spin wave function is antisymmetric, because ψ_α is symmetric.

23. Heitler and London, "Wechselwirkung neutraler Atome" (ref. 1), 460–63, on 462.

24. Werner Heisenberg, "Mehrkörperproblem und Resonanz in der Quantenmechanik," *ZP* 38 (1926): 411–26. On the origins of the resonance concept in physics and its use in chemistry, see Cathryn Carson, "The Peculiar Notion of Exchange Forces—I: Origins in Quantum Mechanics, 1926–1928," *SHPMP* 27 (1996): 23–45; Park, "Chemical Translators" (ref. 5). On Heisenberg's study of helium, see Jagdish Mehra and Helmut Rechenberg, *The Historical Development of Quantum Theory, Vol. 3: The Formulation of Matrix Mechanics and Its Modifications, 1925–1926* (New York: Springer-Verlag, 1982), 282–301.

25. Heitler and London, "Wechselwirkung neutraler Atome" (ref. 1), 461. For Heitler and London's concern about (mis)interpretation of exchange effect, see Gavroglu and Simões, "The Americans, the Germans" (ref. 4), 61–65.

By the same token, E_β should be an energy state in which the electrons are in the same orientation (parallel), because ψ_β is antisymmetric. Therefore, the electronic spin state becomes a useful indicator of the molecular formation: the antiparallel spin state leads to attraction (thus, bonding), while the parallel spin state corresponds to the unstable excited state. In other words, the chemical bond results from the pairing of electrons of different spin orientations, and valence is predicated on this pairing. This conclusion established a connection between the spin theory of valence and the Lewis theory of the paired-electron bond, on which London elaborated in his papers of 1928.[26]

The further development of Heitler and London's treatment of the hydrogen molecule went in two directions. On the one hand, two Americans, John Slater and Linus Pauling, applied Heitler and London's interpretative scheme to polyatomic molecules, explaining the directed property of valence with the concept of hybridization and opening up a venue for semi-empirical treatments for complex molecular systems.[27] On the other hand, there were those who attempted to make the Heitler-London approach acceptable quantitatively as well as qualitatively without using empirical information. They calculated the exchange integral, employed physical and chemical insights to narrow the gap between theory and experiment, and developed different kinds of computational schemes.

The first step in this direction was made by Yoshikatsu Sugiura, who came from Japan to Europe to learn the new quantum theory in the late 1920s. Thanks to Max Born at Göttingen, Sugiura had an opportunity to read Heitler and London's paper before its publication. Finding that they did not calculate the exchange integral, Sugiura plunged into this problem. In August 1927, he obtained the solution of the integral E_{12} as a function of the distance between the two atoms through a complex procedure of mathematical manipulation involving a power series expansion.[28] Sugiura showed that the equilibrium separation of H_2 was the same as Heitler and London's value, 0.8Å. But his calculation of the binding energy was 3.2 eV, which was closer to the then-available

26. Heitler and London, "Wechselwirkung neutraler Atome" (ref. 1), 465–681; Fritz London, "Zur Quantentheorie der homöopolaren Valenzzahlen," *ZP* 46 (1928): 455–77; Fritz London, "Zur Quantenmechanik der homöopolaren Valenzchemie," *ZP* 50 (1928): 25–51.

27. Buhm Soon Park, "The Contexts of Simultaneous Discovery: Slater, Pauling, and the Origins of Hybridisation," *SHPMP* 31 (2000): 451–74.

28. Yoshikatsu Sugiura, "Über die Eigenschaften des Wasserstoffmoleküls im Grundzustande," *ZP* 45 (1927): 484–92, on 492 for Born's guidance.

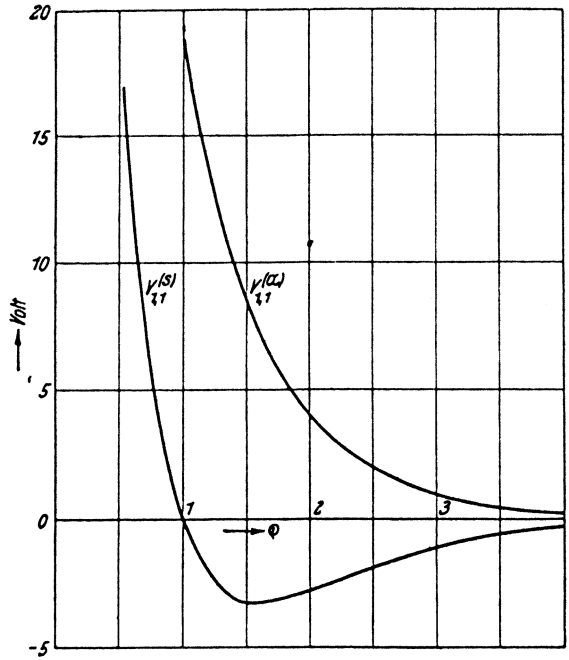

FIG. 2 Sugiura's energy diagram for the hydrogen molecule: Sugiura's notations of $V_{1,1}^{(s)}$ and $V_{1,1}^{(a)}$ correspond to Heitler and London's E_α and E_β. *Source:* Sugiura, "Eigenschaften" (ref. 28), 490. With kind permission of Springer Science + Business Media.

empirical value, 4.4 eV, than Heitler and London's calculation had been. The agreement was, in his opinion, satisfactory.

Shou Chin Wang, a Chinese physicist pursuing his doctorate at Columbia University, also was interested in the problem of the hydrogen molecule. Wang learned quantum mechanics by carefully reading the latest issues of *Zeitschrift für Physik* in a study group led by Ralph Kronig.[29] Wang's approach was basically the same as Heitler and London's, in that he formed a linear combination of wave functions assuming atomic individuality in the molecule.[30] However, Wang attacked the problem with a different mathematical technique. Instead of calculating the perturbation energy, he adopted the variational method, just as Kellner had successfully applied it to the helium problem.

29. Katherine R. Sopka, *Quantum Physics in America, 1920–1935* (New York: Aron Press, 1980), 3.48–3.50, and 3.102.

30. Shou C. Wang, "The Problem of the Normal Hydrogen Molecule in the New Quantum Mechanics," *PR* 31 (1928): 579–86.

Wang was also attracted to Kellner's use of the effective nuclear charge *Ze* as a variable parameter. Putting the effective nuclear charge into the hydrogen eigenfunctions, Wang finally obtained improved results: the equilibrium separation was 0.73Å and the dissociation energy 3.76 eV. On the verge of completing his paper, Wang received the issue of *Zeitschrift für Physik* containing Sugiura's paper. Nevertheless, Wang was confident that his work was worthy of publication since he "used a new method of calculation and arrived at some results in a little better agreement with the experimental data than Sugiura's."[31]

Neither Sugiura nor Wang attempted further improvements to their calculations.[32] But the persistent discrepancy between theory and experiment continued to attract the attention of young scientists like Nathan Rosen. Rosen would become better known as one of the coauthors of the Einstein-Podolsky-Rosen (EPR) paradox, which was devised to criticize the Copenhagen interpretation of quantum mechanics in 1935. But in the early 1930s Rosen worked on the problem of H_2 as a graduate student of Slater at MIT. According to Rosen, previous treatments of this problem were "hitherto successful qualitatively but not quantitatively." He maintained that there should be a better way to inquire into the various complicated interactions between atoms, such as the distortion of the charge distribution. Rosen valued Wang's treatment of this distortion with the altered atomic radius, but to him it remained "rather far from the goal."[33] Noting that atomic interactions might occur along the molecular axis rather than symmetrically about a sphere, he assumed that the electronic cloud of an atom would be polarized or "bulge out" toward its binding partner. His consideration of the "polarization effect" gave an improved value of the binding energy, 4.02 eV.

By the early 1930s, it became apparent that one of the weaknesses of the Heitler-London approach was its neglect of the possibility of ionic configurations in

31. Ibid., 579.

32. After his research trip in Europe, Sugiura returned to Tokyo to join the Institute of Physical and Chemical Research (Riken) established in 1917. Along with Bunsaku Arakatsu and Yoshio Nishina, Sugiura also lectured on quantum mechanics at Kyoto from 1929 to 1931. See Dong-Won Kim, *Yoshio Nishina: Father of Modern Physics in Japan* (New York: Taylor & Francis, 2007); Hideki Yukawa, *Tabibito,* trans. Laurie M. Brown and R. Yoshida (Singapore: World Scientific Publishing, 1982), 176–77. In comparison, Wang continued to study the new quantum mechanics and atomic theory at Wisconsin and Chicago on a National Research Fellowship in 1928–29. Like Sugiura, however, he finally went back to his home country, China, to teach modern physics at the University of Chekiang and later at Beijing University. For Wang's professional career, see *National Research Fellowships, 1929–1944* (Washington, DC: National Research Council, 1944), 37.

33. Nathan Rosen, "The Normal State of the Hydrogen Molecule," *PR* 38 (1931): 2099–114, on 2099.

molecules. Sidney Weinbaum examined this problem under Pauling's guidance at the California Institute of Technology. He added ionic terms to the wave functions originally proposed by Heitler and London, finding an improvement in the binding energy of 0.0031 eV, or three percent over Sugiura's value.[34] He also showed that considering the effective nuclear charge plus the ionic term would yield an improvement of eight percent over Wang's value, a result which was almost equivalent to Rosen's. The addition of Rosen's term into the Wang-ionic treatment turned out to give the best value, 4.10 eV, among the varied ones obtained by Heitler and London's method for setting up the wave function.

In 1933 Hubert M. James and Albert S. Coolidge then obtained by far the most accurate theoretical value by using the coordinate of the interelectronic distance, the method developed by Egil Hylleraas for helium.[35] James and Coolidge were at Harvard University, James as a physics graduate student and Coolidge as a chemistry professor. Both of them learned quantum mechanics from Edwin C. Kemble, a renowned physicist at Harvard, and their initial collaboration took place, at Kemble's suggestion, when they checked each other's calculations for quantum mechanical treatments of the chlorine molecule (by James) and the water molecule (by Coolidge).[36] During his calculations, James found that Cl_2 was too complex to be handled by the Heitler-London method and thus changed his problem to a much simpler one, the lithium molecule. Here he soon realized that "all calculations made up to that time on molecules with inner shells [like Li_2] were unreliable, some apparently good results being due to cancellation of several serious approximations." This time, James looked for a better method of approximation. "I completed this work [on Li_2] in the summer of 1932, while I was on vacation at my home in West Virginia," he recalled. "The result brought me to look for a better method than that of Heitler and London for the treatment of molecules, and I naturally did this in the context of the simplest typical molecule, H_2."[37]

34. Sydney Weinbaum, "The Normal State of the Hydrogen Molecule," *JCP* 1 (1933): 593–96.

35. Hubert M. James and Albert S. Coolidge, "The Ground State of the Hydrogen Molecule," *JCP* 1 (1933): 825–35.

36. In fact, James started his graduate study in the chemistry department in 1928. But after finding that his interests were in mathematics and physics, he switched over to the physics department. For James's switch and Kemble's role in the James-Coolidge collaboration, see Hubert M. James, Response to Early 1930s PhDs Survey, 1980, American Institute of Physics, College Park, MD, MB31142.

37. Hubert M. James to Katherine R. Sopka, 9 May 1972, quoted in Sopka, *Quantum Physics* (ref. 29), 4.87–4.88.

James and Coolidge abandoned the fundamental assumption of Heitler and London's method, i.e., atomic individuality. But they did not adopt the molecular orbital method either, an alternative way of approximating the molecular orbital as a linear combination of atomic orbitals that had been developed by John Edward Lennard-Jones, Robert S. Mulliken, and Friedrich Hund around 1930.[38] Instead of using atomic orbitals, they started with a trial function having many variable parameters:

$$\psi = \sum_{mnjkp} C_{mnjkp}[(1/2\pi)e^{-\delta(\lambda_1+\lambda_2)}(\lambda_1^m\lambda_2^n\mu_1^j\mu_2^k\rho^p + \lambda_1^n\lambda_2^m\mu_1^k\mu_2^j\rho^p)],$$

where λ_1, λ_1, μ_1, and μ_2 were four elliptic coordinates obeying the following relations,

$$\lambda_1 = (r_{1a} + r_{1b})/R,$$
$$\lambda_2 = (r_{2a} + r_{2b})/R,$$
$$\mu_1 = (r_{1a} - r_{1b})/R,$$
$$\mu_2 = (r_{2a} - r_{2b})/R,$$

and the fifth coordinate, $\rho = 2r_{12}/R$, involved the interelectronic distance. The summation in the trial function was to extend over the positive or zero values of the indices, with the restriction that $j + k$ be an even value as required by nuclear symmetry. The function was allowed to include as many terms as necessary to give an acceptable approximation for the energy. To examine the behavior of this function, James and Coolidge fixed the equilibrium distance R at $1.4a_0$ (or 0.74 Å) and the exponent δ at $0.75a_0$, and then solved a set of equations that came from the condition of obtaining values of the coefficients C to minimize the energy.

It turned out that the inclusion of several terms could lead to an energy value much better than any previously reported. As the number of terms increased, there were additional improvements. Yet the computations became more and more laborious, because each new term required the computation of numerous integrals. Nonetheless, the success of James and Coolidge's treatment was immediately recognized, in Pauling and Wilson's words, as a "thoroughly satisfactory treatment of the normal hydrogen molecule, the only improvement

38. The molecular orbital method was based on a different way of describing the wave function $(\psi_1+\varphi_1)(\psi_2+\varphi_2)$. The calculation of hydrogen's binding energy based on this method, however, gave a poorer result (2.68 eV) than Sugiura's. Charles A. Coulson, "The Energy and Screening Constants of the Hydrogen Molecule," *Transactions of the Faraday Society* 33 (1937): 1479–92.

TABLE 1. Quantum-Mechanical Calculations of the Binding Energy and Equilibrium Separation of the Hydrogen Molecule from 1927 to 1933

Type of Wave Function		*Maximum Binding Energy (D_e)*	*Equilibrium Separation (r_e)*
Heitler-London, rough estimation (Heitler and London, 1927)		2.4	0.8
Heitler-London, computed (Sugiura, 1927)		3.14	0.87
Heitler-London with screening effect (Wang, 1928)		3.76	0.73
Heitler-London with screening effect and polarization term (Rosen, 1931)		4.02	0.74
Heitler-London with ionic term (Weinbaum, 1933)		3.21	0.90
Heitler-London with screening effect and ionic term (Weinbaum, 1933)		4.00	0.74
Heitler-London with screening effect, polarization term, and ionic term (Weinbaum, 1933)		4.10	–
Trial Function with the interelectronic coordinate (James and Coolidge, 1933)	one term	2.56	0.74
	five terms	4.507	0.74
	eleven terms	4.682	0.74
	thirteen terms	4.697	0.74
Experiment		4.725	0.74

Source: Van Vleck and Sherman, "Quantum Theory" (ref. 42), 188. The molecular orbital approximation performed poorly even with the consideration of the screening effect. See Coulson, *Valence* (ref. 40), 119.

which we may look forward to being the increase in accuracy by the inclusion of further terms."[39] And their paper was praised for showing that Schrödinger's equation was reliable for molecules as well as atoms. "It is not unreasonable to claim that their highly laborious calculations, yielding such an excellent final result, represent one of the most satisfactory 'proofs' of the validity of the original wave equation when applied to problems with more than one electron," wrote the British quantum chemist Charles A. Coulson.[40]

James and Coolidge's success was good reason for optimism regarding the possibility that molecular properties could be calculated *ab initio* using only the Schrödinger equation plus a few fundamental constants (such as the electronic charge and mass and Planck's constant) and the atomic number and the masses

39. Pauling and Wilson, *Introduction* (ref. 13), 351.

40. Charles A. Coulson, *Valence* (Oxford: Oxford University Press, 1952), 118. See also Henry F. Schaefer III, *Quantum Chemistry: The Development of* Ab Initio *Methods in Molecular Electronic Structure Theory* (Oxford: Oxford University Press, 1984), 1–2.

of the nuclei involved, with no further empirical data. In another sense, however, James and Coolidge's success was equal reason for pessimism: the amount of computation was monumentally formidable. Thus a textbook of quantum chemistry from the 1940s noted:

> [T]he labor involved in these calculations is so great even for these simple systems [such as He, H_2^+, and H_2] that it does not appear to be a profitable method of attack on molecular problems in general. Because of the mathematical difficulties involved, we are forced to use much less accurate approximations; usually we are forced to write the wave function as some linear combination of one-electron wave functions. Although these will not give satisfactory quantitative results, they should in general be qualitatively correct, and should enable us to correlate experimental chemical facts.[41]

As James found, the good fortune of unjustified approximations could provide remarkably good results for diatomic molecules, such as Li_2, LiH, Na_2, K_2, and KH.[42] One common assumption was to consider only the valence electrons (that is, to ignore the other electrons in the closed inner shells) when dealing with the binding energy of molecules larger than hydrogen. Neglecting inner-shell electrons led to a nice agreement between calculated and observed values of the binding energy of Li_2, but James showed that considering inner-shell electrons would completely destroy the agreement. The rigorous treatment gave poorer results than the rough one! This was called "the nightmare of inner shells."[43] In fact, James proposed a remedy: describe valence electrons with the same function as he and Coolidge had devised for hydrogen, and treat nonvalence electrons by means of simple atomic orbitals. However, the computational difficulties in this procedure, especially considering r_{12} terms in the presence of other electrons, were insurmountable. James could only conclude: "In principle, then, we appear to have a way in which to treat diatomic molecules with any desired precision. Unfortunately, the limits of human patience restrict the usefulness of the complete method."[44]

41. Henry Eyring, John Walter, and George E. Kimball, *Quantum Chemistry* (New York: John Wiley & Sons, 1944), 217.

42. Hubert M. James, "Wave-Mechanical Treatment of the Li2 Molecule," *JCP* 2 (1934): 794–810; Hubert M. James, "Wave-Mechanical Treatment of the Molecule Li_2^+," *JCP* 3 (1935): 9–14. See also John H. Van Vleck and Albert Sherman, "The Quantum Theory of Valence," *RMP* 7 (1935): 167–228.

43. Van Vleck and Sherman, "Quantum Theory" (ref. 42), 185–86.

44. Ibid., 186–90, on 190. This part of the review article was written by James, according to footnote 37 of Van Vleck and Sherman's article.

James and Coolidge continued their collaboration until 1940, working on polyatomic molecules, but with no notable success.[45] Their research program demanded intensive labor with the computing facilities then available. It was only after the war that electronic digital computers reopened the field of rigorous calculations of molecular properties by significantly relieving human labor.[46] As a result, James and Coolidge's work is often seen as paradoxically heralding the coming of the "dark ages" for the *ab initio* method, which would last for more than a decade.[47] The H_2 problem, the simplest molecular system, served as a test case for the level of accuracy that could be achieved by adding more correction terms and putting in more computational labor. In hindsight, that was at least a manageable molecular system for young graduate students and postdocs who had just entered the field of quantum theory.

CRITERIA FOR GOOD APPROXIMATIONS

In order to make quantum mechanics applicable to more complex atomic and molecular systems, some kind of trade-off between manageability and accuracy was required. The less accurate results one could afford, the more manageable the problem became. An insightful approximation method in this regard was developed for multi-electron atoms by the British mathematical physicist Douglas R. Hartree in 1928. Hartree's approach was called the self-consistent-field (SCF) method. A version of the SCF method for molecules became available a few decades later. As it turned out, the SCF method was less accurate but much more manageable than Hylleraas's, and it was more laborious but much more reliable than the method of using just analytical functions.

45. James, Response, 1980, AIP (ref. 36). In 1940, James became an assistant professor at Purdue University, where his interests were diverted to polymer and solid-state physics.

46. Buhm Soon Park, "The 'Hyperbola of Quantum Chemistry': The Changing Identity and Practice of a Scientific Discipline in the Early Years of Electronic Digital Computers, 1945–65," *Annals of Science* 60 (2003): 219–47.

47. Schaefer, *Quantum Chemistry* (ref. 40), 4. Indeed the quantitative investigation of molecules, being limited to relatively simple ones, languished in the late 1930s and 1940s. Only a small number of studies on the hydrogen molecule (seven) were reported in this period, and all of them, using various trial functions, fell short of the accuracy of James and Coolidge's. See A. D. McLean, A. Weiss, and M. Yoshimine, "Configuration Interaction in the Hydrogen Molecule—The Ground State," *RMP* 32 (1960): 211–18; Andrea I. Woody, "Early Twentieth-Century Theories of Chemical Bonding: Explanation, Representation, and Theory Development (Quantum Chemistry)" (PhD dissertation, University of Pittsburgh, 1997).

Douglas Hartree was first and last a Cambridge man: born and educated in Cambridge, teaching there for much of his professional career, and now buried there.[48] He excelled in mathematics at St. John's College, graduating in 1921 with First Class Honors in Part I of the Mathematical Tripos and Second Class Honors in Part II of the Natural Sciences Tripos. Hartree continued his graduate study in Cambridge under the Plummer Professor of Mathematical Physics, Ralph H. Fowler. A highlight of that time was Bohr's visit to Cambridge in 1921. Immediately attracted to the quantum theory as presented by one of its authors, Hartree began to explore the electronic structure of atoms. It was a problem that Bohr handled only qualitatively. If Bohr's theory was right, Hartree pondered, could one find an electric field for the atom—the field in which one could draw the actual form of the orbits and track the course of time along them, and, furthermore, in which one could calculate the energy levels of states matching experimental data? In 1923 Hartree sought to answer this question in his paper, "On Some Approximate Numerical Applications of Bohr's Theory of Spectra."[49]

As Hartree set out in the introduction, the paper contained the germ of the idea of the self-consistent field:

> For various reasons a type of field is assumed much simpler than the actual atomic field must be, and exact agreement between all calculated and observed terms is not to be expected and cannot in fact be obtained, but good enough agreement is obtained to make the quantitative results interesting; and both for the dimensions of the orbits and for the field they probably form a fairly good first approximation. The orbits of the electrons normally present in the atom having been calculated, the field due to them could be determined and compared with the field deduced from the spectral terms.[50]

48. Charlotte F. Fischer, *Douglas Rayner Hartree: His Life in Science and Computing* (London: World Scientific Publishing, 2004); C. G. Darwin, "Douglas Rayner Hartree," *Biographical Memoirs of the Fellows of the Royal Society* 4 (1958): 103–16; R. B. Lindsay, "Douglas Rayner Hartree," in *Dictionary of Scientific Biography*, vol. 6, ed. Charles C. Gillispie (New York: Charles Scribner's Sons, 1970), 147–48. See also Ana Simões and Kostas Gavroglu, "Quantum Chemistry in Great Britain: Developing a Mathematical Framework for Quantum Chemistry," *SHPMP* 31 (2000): 511–48, esp. 515–20. For the tradition of mathematical physics at Cambridge University see Warwick, *Masters of Theory* (ref. 7).

49. Douglas R. Hartree, "On Some Approximate Numerical Applications of Bohr's Theory of Spectra," *PCPS* 21 (1923): 625–41; Simões and Gavroglu, "Quantum Chemistry" (ref. 48), also note the importance of Hartree's 1923 paper in the development of the idea of the self-consistent field.

50. Hartree, "Bohr's Theory of Spectra" (ref. 49), 625.

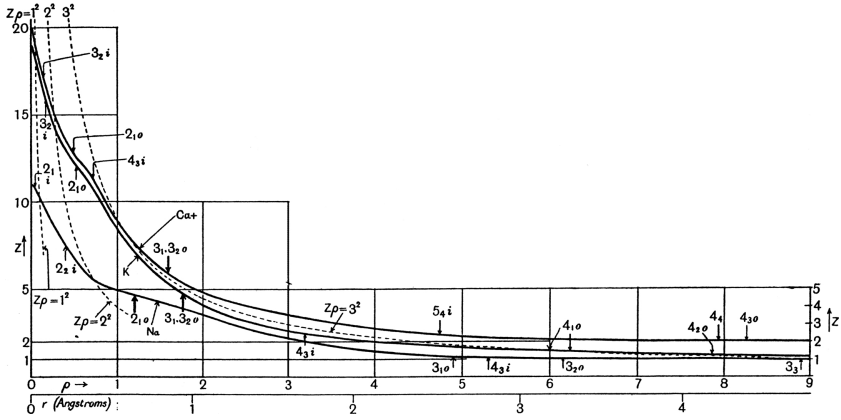

FIG. 3 Hartree's early idea of the SCF method. (Z, ρ) curves for Na, K, Ca^+, determined by analysis of optical and x-ray spectral terms. Z is the effective nuclear charge, and ρ is the distance from nucleus in Bohr's atomic unit (that is, r/a, where a is the radius of hydrogen). The full line curves are the curves of Z as a function of ρ. The broken curves are the hyperbolae $Z\rho = k^2$ (k, the radial quantum number, is the integer). *Source:* Hartree, "Bohr's Theory of Spectra" (ref. 49), 634. With kind permission of Cambridge University Press.

His logic was clear: (1) assume a simple type of field (here, a central field, i.e., a function only of the distance r from the nucleus); (2) impose quantum conditions; (3) express the effective nuclear charge Z as a function of r, and solve the integral for the field, $V(V = \int^{\infty} Z/r^2 dr)$; (4) compare the obtained field with the experimental one, to see if they are consistent. In reality, however, Hartree could not obtain the atomic field from the theory alone. Instead, he worked backwards, reversing steps (3) and (4): he put empirical energy terms into the equation obtained from the quantum conditions, and then found Z as an empirical function of r. Since the Z function was given only in graphical or tabular form, the final integration had to be carried out numerically.

Hartree's method here was semi-empirical. But within the framework of the old quantum theory, there were not many alternatives for getting a quantitative picture of the electric field of atoms.[51] Moreover, his study indicated a notable paradox of the Bohr theory: the electrons moving *in sharply defined orbits*

51. Ibid. Hartree acknowledged that Erwin Fues did similar calculations independently, but argued that his own method was more general than Fues's. In 1924, R. B. Lindsay sought to derive a charge density straightforwardly from a spherical average of Bohr orbits, which Slater saw as a step closer to the self-consistent-field method. See John C. Slater, *Solid-State and Molecular Theory: A Scientific Biography* (New York: John Wiley & Sons, 1975), 53. On the relationship that developed between Hartree and Lindsay in the 1930s, see Simões and Gavroglu, "Quantum Chemistry" (ref. 48), 527–28.

produced a *smooth charge distribution curve*, which went quite a long way outside the boundary of the atom.[52] This was explained only after the arrival of quantum mechanics.

Hartree was awarded his PhD in 1926, but he stayed in Cambridge as a Fellow of St. John's College and of Christ's College until he took the Chair of Applied Mathematics at Manchester in 1929. It was during his postdoctoral period that Hartree developed a quantum-mechanical method of investigating the electronic structure of atoms.[53]

The overall structure of Hartree's new method looked similar to that of his old one. First of all, Hartree started by assuming a central field (a function of r only), which he called the initial field. He then corrected the field for each electron, as the distributed charge of an electron must be omitted in finding the field acting on it. The third step was to put this corrected field into the Schrödinger equation and solve it for each electron. From the solutions for all electrons, a distribution of charge could be calculated. Hartree then found the field of the nucleus together with this charge distribution, the final field. In short, the whole process could be expressed in diagrammatic form: "Initial Field → Initial Field corrected for each core electron → Solutions of Wave Equation for core electrons → Distribution of Charge → Final Field."[54] If the final field was the same as the initial one, the field would be called "self-consistent," and no more numerical work would be necessary. If not, the procedure should be repeated by taking the final field of the first approximation as the initial field of the second one, over and over again, until self-consistency would be achieved.

Therefore, unlike the old quantum theory, quantum mechanics enabled Hartree to obtain the atomic charge distribution without using any empirical data. He needed no input of spectral information to calculate the energy level of atoms. The SCF method was nonempirical, *ab initio*. As an example, Hartree

52. Hartree, "Bohr's Theory of Spectra" (ref. 49), 639. See also Slater, "Electronic Structure" (ref. 15), 485.

53. Douglas R. Hartree, "The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part I: Theory and Methods," *PCPS* 24 (1928): 89–110; Douglas R. Hartree, "The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part II: Some Results and Discussion," *PCPS* 24 (1928): 111–32; Douglas R. Hartree, "The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part III: Term Values and Intensities in Series in Optical Spectra," *PCPS* 24 (1928): 426–37; Douglas R. Hartree, "The Wave Mechanics of an Atom with a Non-Coulomb Central Field. Part IV: Further Results Relating to the Optical Spectrum," *PCPS* 25 (1929): 310–15.

54. Hartree, "Part II" (ref. 53), 111–14, on 113. See also Simões and Gavroglu, "Quantum Chemistry" (ref. 48), 517–18.

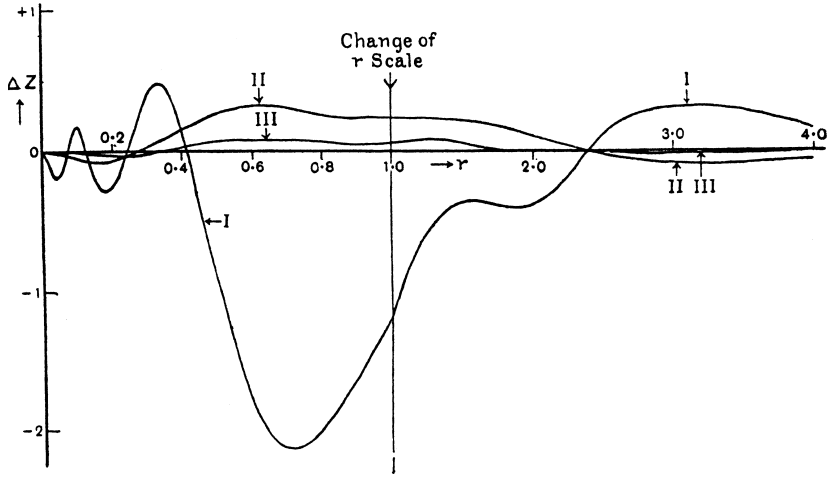

FIG. 4 Hartree's three approximations to SCF for Rb. Difference (ΔZ between effective nuclear charge of initial and final field was plotted against r for the three approximations (Curves I, II, and III). *Source:* Hartree, "Wave Mechanics. Part II" (ref. 53), 118. With kind permission of Cambridge University Press.

showed how successive approximations narrowed the difference between the effective nuclear charge of initial and final fields for rubidium (Rb), an atom having thirty-seven electrons.[55]

In general, Hartree was satisfied with the agreement between the SCF calculations and observed values for He, Rb, Rb^+, Na^+, and Cl^-: for instance, the calculated ionization potential of helium was 24.85 eV, just 0.2 eV away from the observed value. He regarded this "very close agreement" as an "empirical justification of the simple approximations," even a "notable success of the method."[56] Convinced of the usefulness of his approximation method, which did not require "very much more elaborate theoretical and numerical work," he was hopeful that "when the time is ripe for the practical evaluation of the exact solution of the many-electron problem, the self-consistent fields calculated by the methods given here may be helpful as providing first approximations."[57]

Only a few months after the publication of Hartree's papers in 1928, J. A. Gaunt of Trinity College offered a critical review.[58] Gaunt's purpose was not

55. Hartree, "Part II" (ref. 53), 117–18.

56. Ibid., 117.

57. Ibid., 114.

58. J. A. Gaunt, "A Theory of Hartree's Atomic Fields," *PCPS* 24 (1928): 328–42. Schweber, "Young John Clarke Slater" (ref. 4), also notes critical comments on the Hartree method by Gaunt and Slater.

to disprove the SCF method, but to assess Hartree's assumptions in light of recent developments in quantum mechanics. He saw the assumptions as "simple and picturesque," yet "open to several objections" from a rigorous point of view. In particular, he raised a question as to whether it was really justifiable to describe the many-electron atom as the simple product of one-electron wave functions of individual electrons, rather than as one complete wave function. This was the fundamental assumption that Hartree himself did not seriously question; in dealing with many-electron systems Hartree did not even consider the Pauli exclusion principle, the spin state of electrons, or Heisenberg's resonance phenomenon. In this regard, Hartree's method was flawed. Investigating the error possibly caused by the neglect of resonance terms, however, Gaunt showed that the terms attributable to resonance were small enough. Indeed, he found that Hartree's method gave a better result for helium's ionization potential than the perturbation method. Thus he concluded: "Hartree's wave functions have been shown to be good approximations."

A more thorough review of Hartree's papers came from John Slater.[59] Like Gaunt, Slater stressed that Hartree should have considered the resonance interactions between electrons. In addition, Slater pointed out, Hartree also neglected that electron distributions were not really spherical. This was in fact what Hartree had been most concerned about. He had been aware that except for an electron in an *s* orbit (with azimuthal quantum number $l = 0$), the electron's own contribution to the field was not spherically symmetrical, and thus that the assumption of a central field had no general applicability. "It was just here," Hartree had admitted, "that we meet the most serious doubts concerning the replacement of the actual many-body problem by a one-body problem with a central field for each electron, even as a first approximation."[60] Besides, Slater found an inconsistency in Hartree's method of dealing with the core (inner-shell) electrons and the valence electron: for the valence electron, he solved the problem of the core electrons first and used the central field determined from it, thus neglecting the influence of the valence electron on the core electrons. In other words, Hartree neglected the possible polarization of the inner shell by the valence electron.[61]

Slater's criticism was not geared toward invalidating the SCF method. Instead, by estimating the errors in it, Slater sought to provide a theoretical justification

59. John C. Slater, "The Self Consistent Field and the Structure of Atoms," *PR* 32 (1928): 339–48.

60. Hartree, "Part II" (ref. 53), 112.

61. Slater, "Self Consistent Field" (ref. 59), 346–48.

for Hartree's approximation method. Thus his conclusion was not much different from Gaunt's: "We see that none of the corrections to Hartree's terms are really much larger than the order of magnitude of his discrepancies from experiment, so that his good agreement with observation is justified."[62] Hoping that Hartree would not misinterpret his criticism, Slater sent him a draft of his paper. In reply, Hartree wrote: "I certainly hope you will publish this paper. . . . Certainly I do not feel at all that you are treading on my toes in working on this subject; on the contrary I am very glad the problem has attracted you, and that you and Gaunt have been able to justify the procedure I adopted empirically. If you want to do any further work involving numerical values," he added, "I would be glad to send you any numerical data I possess."[63]

Slater gave his critical review of the SCF method in 1928, when his main interest was moving from radiation problems to the theory of matter—atoms, molecules, and metals.[64] Slater was seeking the proper way of incorporating Pauli's exclusion principle in treatments of many-electron atoms, as Heisenberg had done for helium with the concept of resonance. In fact, many competent theoretical physicists, such as Heitler, Eugene Wigner, Frederick Hund, and Herman Weyl had been engaged with this problem since Heisenberg's helium paper was published in 1926. They followed the procedure Heisenberg had prescribed: first they tried to find the appropriate form for the wave functions of the ordinary position coordinates (x, y, z), and then they considered the spin needed to make the whole wave function antisymmetric with respect to the exchange of electrons. To this end, they used group theory. In contrast, Slater took the opposite tack, introducing the spin at the very beginning of the calculation. This led to a much simpler way of representing the antisymmetric wave function, now known as the determinantal method.[65]

In developing the determinantal method, Slater owed much to Hartree. Slater profited from the analysis of Hartree's papers, from which he learned that the assumption of a central field in many-electron atoms worked out well,

62. Ibid., 348.

63. Douglas R. Hartree to John C. Slater, 6 Jul 1928, JSP, D. R. Hartree, #1.

64. Slater took his doctoral degree at Harvard University in 1923 under the supervision of the experimental physicist Percy W. Bridgman, writing a thesis on the compressibility of alkali halide crystals of the sodium chloride type. So it is possible to see that Slater was moving back to his earlier interest. But he also felt that he was outpaced by Dirac, who published a paper on quantum electrodynamics that was far more comprehensive and thorough than Slater's ideas. See Schweber, "Young John Clarke Slater" (ref. 4), 373.

65. John C. Slater, "The Theory of Complex Spectra," *PR* 34 (1929): 1293–322.

and the one-electron approximation might be a good starting point even if resonance were neglected. Hence, Slater adopted the central-field assumption, making a slight modification for simplicity of description: "According to [Hartree's scheme], each electron moves in a field of force slightly different from the others. We shall neglect the difference, assuming that all the electrons move in precisely the same field. And this field is to be so chosen as to give the best agreement with the correct values even without further corrections."[66] Slater then used the one-electron approximation, representing each electron's wave function with both position and spin coordinates. As Slater acknowledged, the process of building up the antisymmetric wave function with a determinant was well known.[67] What was new in his method was to represent each electron's wave function with the position and spin coordinates together, and to construct the antisymmetric wave function as the linear combination of the one-electron approximations. Slater's previous study of Hartree's one-electron approximation provided him with the confidence that this kind of approximation would lead to a good result. And he demonstrated the validity of his method by using it in the wave-mechanical study of complex atomic spectra, most notably the theoretical explanation of Hund's empirical rule for classifying spectra.

Slater sent his paper on "The Theory of Complex Spectra" to the *Physical Review* shortly before he took a trip to Europe in the summer of 1929 as a Guggenheim Fellow. Everyone he met seemed to know of his work, and most of them liked it. "No other work I have done," Slater wrote in his autobiography, "was so universally popular." The paper was particularly welcomed by those physicists who saw group theory as arcane, incomprehensible mathematical manipulation; he later heard such remarks as "Slater had slain the 'Gruppenpest' [the pest of group theory]."[68] He met Hartree at a conference in Zurich, before going to Leipzig to spend half a year with Heisenberg and Hund.

In Leipzig, however, Slater found that Hartree's self-consistent-field method was not well received among the quantum theorists. Despite some theoretical

66. Ibid., 1299. On the influence of Hartree's work on the development of Slater's determinantal method, see also Schweber, "Young John Clarke Slater" (ref. 4), 375–77; Simões and Gavroglu, "Quantum Chemistry" (ref. 48), 519.

67. Slater, "Theory" (ref. 65), 1294. Slater mentioned Dirac's earlier papers and the recent paper by Iva Waller and Douglas R. Hartree's "The Intensity of Total Scattering of X-rays," *PRS* A124 (1929): 119–42.

68. Slater, *Solid-State and Molecular Theory* (ref. 51), 62–63. Slater noted the responses from Hund, Waller, Hartree, Bloch, Heisenberg, and Wigner. See also Schweber, "Young John Clarke Slater" (ref. 4), 377.

justifications given by Gaunt and Slater, many still considered the SCF method to "stand apart from the main current of quantum theory" and "to contain arbitrary and empirical elements." Thus Slater sent a short note to the *Physical Review* in defense of the SCF method.[69] This time he insisted upon its close relation to the procedure a scientist should take when applying the variational principle to the simple product of one-electron wave functions. He wrote:

> Suppose one sets up an approximate wave function for a general problem of the motion of electrons among stationary nuclei, by assuming a product of functions of the various electrons: $u = u_1(x_1) \ldots u(x_n)$; suppose further that one apply the variation principle by varying separately each of the functions u_i, leaving the others constant. The n variation equations so obtained prove to be those for the motion of the n electrons, each in a separate electrostatic field; and the field for each electron is obtained by adding the densities u_i^2 for all the other electrons, and finding by electrostatics the field of this charge and of the nuclei. Thus this field is self-consistent in the sense of Hartree; the result is a generalization of his method to more complicated problems than atomic ones.[70]

The variational scheme was designed to find the best approximate wave function by varying arbitrary parameters or arbitrary functions so that the energy of the system was stationary with respect to slight variations. Slater realized that this way of finding the best approximate wave function was tantamount to finding the self-consistent field: that is, the best function would lead to the self-consistent field, or vice versa. One notable difference in practice was that the variational procedure did not include the spherical averaging of potential. Hartree needed this step to compare the initial and final fields in terms of the actual charge distributions of those fields; but in the variational procedure, the comparison was made by the convergence of the energy in the successive variations of the initial trial wave function.

In his note, Slater also hinted that the exclusion principle could be considered in the SCF method by using his determinantal representation of the antisymmetric function. Yet he did not show how to set up an elaborate formulation for applying the variational principle to the antisymmetric function. A few months later, the Russian physicist Vladmir Fock developed another way of formulating the SCF method with the variational principle. Unfamiliar with Slater's determinantal method, Fock used the technique of the permutation

69. John C. Slater, "Note on Hartree's Method," *PR* 35 (1930): 210–11, on 210.
70. Ibid., 211.

group—hence, the Hartree-Fock (instead of the Hartree-Slater-Fock) method.[71] Finally, in 1935, Hartree simplified Fock's formulation with Slater's determinantal method.[72]

The Hartree-Fock method was universally accepted, not because it produced results as accurate as those Hylleraas had achieved with helium, but because it provided a manageable tool for handling heavy atoms. From the beginning, it was realized that this method was only of limited accuracy, giving errors of around one percent. The source of the errors was also well known: the neglect of electron correlation. Hartree's original SCF method presumed that electrons moved completely independently of each other; and Fock's elaboration remedied this problem partially, only through the requirement of antisymmetry of wave function. This kind of electron correlation was regarded as accidental, since it stemmed from the Pauli principle rather than from the electrostatic requirement that the electrons should keep away from one another. The further refinement of the Hartree-Fock method was thus to consider electron correlation in a more general way.[73] Despite this problem, there was a consensus that Hartree-Fock approximations were the "best possible" one-electron wave functions, and that these were "the only wave functions which can be used in most problems concerning the energy levels of complex systems."[74]

Although the idea of the self-consistent field was central to Hartree's original method or its modified form, Hartree's genius lay in his numerical analysis of difficult wave equations. For each cycle of approximations, and for each electron, he had to solve the differential equation that was a function of radial distance from the nucleus r, which could not be done analytically. So Hartree developed a technique of numerical integration, basically a way of solving the equation at numerous fixed points of r; and, in fact, computations took up so much of his energy that he failed to keep abreast of developments in quantum

71. Vladmir Fock, "Näherungsmethode zur Lösung des Quantenmechanischen Mehrkörperproblems," *ZP* 61 (1930): 126–48. The paper was received on 21 Feb 1930. In it, Fock made no mention of Slater's work, although he cited Gaunt's paper on Hartree's method.

72. Douglas R. Hartree and William Hartree, "Self-Consistent Field, with Exchange, for Beryllium," *PRS* A150 (1935): 9–33. See also Douglas R. Hartree, "Theory of Complex Atoms," *Nature* 138 (1936): 1080–82.

73. For the source of the errors in the SCF method, see Frederick Seitz, *The Modern Theory of Solids* (New York: McGraw-Hill, 1940), 237. See also Slater, "Electronic Structure" (ref. 15), 480.

74. Eyring, Walter, and Kimball, *Quantum Chemistry* (ref. 42), 166.

mechanics. In reply to Slater's criticism in 1928, he wrote: "Some of the steps were not clear to me without a bit of work and looking up the general theory, but that is my fault; my time has been so taken up with the development of the numerical technique of evaluating the self-consistent field, and with the actual computing of particular cases, that I am not as familiar as I should be with the general theory outside what I have required for my work, which is not much."[75]

In the 1930s Hartree was fortunate to have the assistance of his father, William Hartree, who liked doing the computing as a way to occupy himself in retirement.[76] Hartree also looked for computing machines to relieve human labor. In the early 1930s, he visited MIT to learn about Vannevar Bush's differential analyzer;[77] and upon his return to Britain, he set up his own model of a differential analyzer with Meccano parts (children's toys) to demonstrate how it worked. After World War II, he again made a trip to America to familiarize himself with the ENIAC (Electronic Numerical Integrator And Computer), the electronic digital computer built for the purpose of calculating the trajectories of projectiles during the war. On his return, Hartree published more than a dozen very detailed reports on this machine for the general public as well as for the scientific community, and he lent his expertise to the installation of digital computers in Britain, including the EDVAC (Electronic Discrete Variable Automatic Computer) in Cambridge and the Ferranti in Manchester. Indeed, popularizing computers and their application to scientific problems became his major activity for several years after he returned to Cambridge in 1946 to succeed Fowler as Plummer Professor of Mathematical Physics. It is no surprise that the title of his inaugural lecture was "Calculating Machines, Recent and Prospective Developments."[78]

75. Hartree to Slater, 6 Jul 1928, JSP (ref. 63).

76. Douglas R. Hartree to John C. Slater, 1 Nov 1939, JSP, D. R. Hartree, #1.

77. Perhaps it was Slater who provoked Hartree to pay a visit to MIT. In one letter to Hartree, Slater gave a description of Bush's differential analyzer, saying he planned to use this machine in the SCF calculations. John C. Slater to Douglas R. Hartree, 25 Nov 1931, JSP, D. R. Hartree, #1.

78. Douglas R. Hartree, *Calculating Machines, Recent and Prospective Developments* (Cambridge: Cambridge University Press, 1947). Thirteen out of Hartree's forty publications after 1946 were intended to inform readers of various journals and government officials about calculating machines. For Hartree's role in the introduction of computers in England, see Mary G. Croarken, "The Emergence of Computing Science Research and Teaching at Cambridge, 1936–1949," *AHC* 14 (1992): 10–15; Paul A. Medwick, "Douglas Hartree and Early Computations in Quantum Mechanics," *AHC* 10 (1988): 105–11.

COMPUTATIONS IN THE HISTORY OF QUANTUM THEORY

Hartree's deep interest in improving calculation techniques and easing human labor did not earn him much respect among quantum physicists. Slater found this unfair. He remarked: "Douglas Hartree was very distinctly of the matter-of-fact habit of thought that I found most congenial. The hand-waving magical type of scientist regarded him as a 'mere computer.' Yet he made a much greater contribution to our knowledge of the behavior of real atoms than most of them did."[79] Slater went on to argue that Hartree's contributions should be seen in a broader context: "While he limited himself to atoms, his demonstration of the power of the self-consistent field for atoms is what has led to the development of that method for molecules and solids as well." Indeed, a convenient method of dealing with molecular problems was developed in the early 1950s by adapting the procedure of the self-consistent-field approximation.[80]

Yet Hartree was not alone in having to cope with the prejudice against computation-oriented research. Sugiura also failed to impress even Heitler. "It appears that there are in the world some hard working dwarfs," Heitler confided to London. "But—honestly now—would *we* be able to manage it at all? . . . It seems to me ridiculous, especially if one sees what kind of perturbation calculation has been done."[81] Heitler certainly put more value on gaining physical explanations than on having exact computations. Heitler's attitude was not much different from Heisenberg's. After finishing his path-breaking paper on helium, Heisenberg remarked: "I am convinced that the spectra of all chemical elements can be obtained . . . from quantum mechanics in a unique manner without physics [i.e., physical insights] by bone-headed calculation."[82]

To a large extent, the historical significance of computation in quantum mechanics has been undervalued or unexplored. How much, then, do we have to

79. Slater, *Solid-State and Molecular Theory* (ref. 51), 54. Slater held that there were two quite different types of thinkers among theoretical physicists. "One type is the prosaic, pragmatic, matter-of-fact sort, who indicates the argument behind what he does, and tries to write or speak in the most comprehensible manner possible. The other is what we might call the magical or hand-waving type, who, like a magician, waves his hands as if he were drawing a rabbit out of a hat, and who is not satisfied unless he can mystify his readers or hearers." Interestingly, Slater believed that Heisenberg and Schrödinger, as well as Hartree, belonged to the first group, and that Dirac was definitely among the second group. See ibid., 42.

80. Clemens C. J. Roothaan, "New Developments in Molecular Orbital Theory," *RMP* 23 (1951): 61–89. See also Park, "Hyperbola" (ref. 46).

81. Walter Heitler to Fritz London, Sep 1927, quoted in Gavroglu, *Fritz London* (ref. 19), 47.

82. Werner Heisenberg to Pascual Jordan, 28 Jul 1926, quoted in Mehra and Rechenberg, *Historical Development* (ref. 24), 301.

pay attention to those "hard working dwarfs" or "bone-headed" computers? Where is their proper place in the history of quantum physics and chemistry? As long as we confine ourselves to the conceptual development of quantum mechanics, it will be difficult to find answers to these questions. A clue can be found in the practice of theory to make incremental improvement or circumvent technological or even conceptual constraints. In this respect, the following two recollections are illustrative. Heitler described his "Eureka!" moment as something akin to a sleepwalking experience:

> I slept till very late in the morning, found I couldn't do work at all, had a quick lunch, went to sleep again in the afternoon and slept until five o'clock. When I woke up . . . I had clearly . . . the picture before me of the two wave functions of two hydrogen molecules joined together with a plus and minus and with the exchange in it. So I was very excited, and I got up and thought it out. As soon as I was clear that the exchange did play a role, I called London up, and he came to me as quickly as possible. Meanwhile I had already started developing a sort of perturbation theory. We worked together then until rather late at night, and then by that time most of the paper was clear. . . . Well . . . at least it was not later than the following day that we had the formation of the hydrogen molecule in our hands, and we also knew that there was a second mode of interaction which meant repulsion between two hydrogen atoms—also new at the time—new to chemists, too.[83]

Heitler and London may have finished essential parts of their paper almost overnight. By contrast, a widely circulated rumor had it that James and Coolidge spent three years on the hydrogen problem—in fact, it took about half a year. But had they had no previous experience of computations with Li_2, Cl_2, and H_2O, it would certainly have taken longer than that. James later remarked:

> The idea of applying to H_2 a treatment analogous to that of the helium atom by Hylleraas came to me in the bathtub—in keeping with the tradition of Archimedes, but with less evident relevance. I made some general notes on the project while I was at home, but I did not have facilities there to begin the calculation. I was familiar enough with molecular calculations to realize how much labor would be involved, and my earlier cooperation with Coolidge had made evident the great advantages of collaboration in such complex numerical calculations. When I returned to Cambridge in the fall of 1932 I discussed with Professor Kemble the possibility of undertaking this project in collaboration with Coolidge.[84]

83. Walter Heitler, interview by J. L. Heilbron, 18 Mar 1963, Archive for the History of Quantum Physics, quoted in Gavroglu, *Fritz London* (ref. 19), 45.

84. James to Sopka, *Quantum Physics* (ref. 37).

Working with machines that seem primitive by today's standards (they started with hand-powered desk calculators and later used motor-driven ones), they found it delightful to get good results after their labor-intensive calculations. "I remember," James said, "as among the happiest and most exciting days of my life the period in which we saw the numerical results come out better and better as we added more and more terms to our calculation."[85] James's "Eureka!" moment had arrived with the realization that enormous labor would be required to carry out his idea, but he received his reward when the theoretical values moved ever closer to the experimental ones.

Shortly after the advent of quantum mechanics, several approximation methods were developed to solve the many-electron Schrödinger equation, but there were considerable difficulties in carrying out the computational work. As Per-Olov Löwdin, a Swedish quantum chemist, quipped in the 1950s: "It is sometimes said that a theoretician is a person who knows how to solve a problem, but who cannot do it."[86] Sugiura, James, Hartree, and other proponents of *ab initio* were those who did it. To them, making a theory really work in atomic and molecular domains was as important as developing one in the first place. Computational imperatives in the early years of quantum chemistry clearly reveal the emerging practice of theory that required human labor, technological improvement (computers), and mathematical ingenuity. In no small measure, this practice contributed to demonstrating the validity of quantum mechanics and its usefulness.

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85. Ibid.

86. Per-Olov Löwdin, "Recent Simplifications in the Molecular Orbital Theory of Calculating Energy Levels," *Proceedings of the International Conference of Theoretical Physics* (Tokyo: Nippon Bunka Insatsusha Company, 1953), 599–609, on 599.