1 Computational Imperatives in Quantum Chemistry

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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 the formulation of a new mechanical system. This is usually introduced as one of the exemplary problems that quantum mechanics solved, thereby validating its general applicability. Singularly recognized as ground-breaking is Walter Heitler and Fritz London's 1927 paper, which gave a theoretical explanation of why two hydrogen atoms combine to form a molecule.[1] Thereafter, Heitler and London were optimistic about understanding the whole territory of chemistry with quantum mechanics, and their reductionist ideal was shared by other physicists, including P. A. M. Dirac, who made a famous 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."[2] Indeed, the excitement about the new theoretical framework was abound 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." According to him, Heitler and London's work "eventually brought the whole of chemistry under the sovereignty of quantum mechanics."[3]

Intriguing is the fact that historians of quantum physics, including Jammer, have paid little attention to whether the reductionist program worked well or faced difficulties in chemistry after 1927. They tend to believe that quantum chemistry, a new field of study that came into being after Heitler and London's paper, would successfully carry the mission of reducing chemistry to physics. Historians of quantum chemistry are rather critical of this picture. They have shown that the early optimism about reductionism quickly subsided into pessimism in the 1930s in the face of complexity of chemical systems, and that quantum chemistry was developed into a discipline with diverse methodologies, indigenous languages, and separate institutional bases.[4] To them, the acceptance of quantum mechanics in chemistry does not necessarily mean the re-

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[1] Walter Heitler and Fritz London, "Wechselwirkung neutraler Atome und homöopolare Bindung nach der Quantenmechanik," *Zeitschrift für Physik*, **46** (1927), 455–72.

[2] P. A. M. Dirac, "Quantum Mechanics of Many-Electron Systems," *Proceedings of the Royal Society*, **A123** (1929), 714–33, quote on p. 714.

[3] Max Jammer, The Conceptual Development of Quantum Mechanics, 2nd ed. (College Park, MD: American Institute of Physics, 1989), pp. 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," *Historical Studies in the Physical and Biological Sciences*, **25** (1994), 47–110; Mary Jo Nye, *From Chemical Philosophy to Theoretical Chemistry* (Berkeley: University of California Press, 1993).

duction of one discipline to another. While I agree on this point of view in general, I want to point out that the historians of quantum chemistry have not fully examined, either, the subsequent development of mathematical tools and conceptual devices to solve the Schrödinger equation for multi-electron atomic or molecular systems without using empirical data. This paper aims to reassess the place of the pioneers of *ab initio* methods in the history of quantum physics or quantum chemistry.[5] I first examine who they were, why they got interested in computations, and how they improved agreement between theory and experiment. And then I show that their computation-oriented work was undervalued by some leading scientists, whose attitude has significantly affected the current historiography of quantum physics and chemistry.

Heitler and London's 1927 Paper

In 1927, two German physicists, Walter H. Heitler and Fritz London, published a paper in which they treated the hydrogen molecule with quantum mechanics and studied the source of its binding energy. This paper was quantum mechanics' first step toward chemistry, almost single-handedly creating the new field of quantum chemistry. In view of the significance of this paper, it is interesting to note that the encounter of Heitler and London was incidental, and that their collaboration was short-lived. Both Heitler and London were products of the University of Munich, trained in different areas: London took his Ph.D. in philosophy in 1921 and spent some years in a teaching job before he decided to study theoretical physics under Sommerfeld; and Heitler worked on the theory of concentrated solutions for his doctoral degree, which he got in 1925, and went to Copenhagen to continue his work on physical chemistry with Niels Bjerrum. Their paths converged in 1927 when each of them received the Rockefeller Fellowship 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 the quantum field theory and London into superconductivity.[6]

Heitler and London's basic idea was to regard the molecule as composed of atoms, a view which was not different from the traditional conception of the molecule in chemistry.[7] But Heitler and London adopted it as part of applying the approximation technique known as the perturbation method, which had been developed in celestial mechanics and used in the old quantum theory. Assuming that the atoms were set apart at the infinite internuclear distance, they first approximated the wave function ($\mathbf{\Psi}$) of the hydrogen molecule with known eigenfunctions of the hydrogen atom, $\Psi_1 \varphi_2$, where Ψ_1 was the eigenfunction of electron 1 at nuclei a and φ_2 was that of electron 2 at nuclei b. At this point, the interaction between the atoms could be neglected. However, as the atoms came closer to each other, one could not ignore the interatomic interaction. Heitler and London regarded this interaction among two electrons and two nuclei as the

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[5]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), p. 1.

[6]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).

[7]For reactions to Heitler and London's paper, see Gavroglu, *Fritz London*, pp. 51–3; Gavroglu and Simoes, "The Americans, the Germans, and the Beginnings of Quantum Chemistry," pp. 70–75.

perturbation of the system.

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"). For one could not know which electron was located near which nuclei: that is, the electrons were indistinguishable. 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 $\Psi_1\varphi2$ 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 (overlap integral) was $\int \Psi_1\varphi_1\Psi_2\varphi_2\, d\tau$. Putting these values into the Schrödinger equation, where R is 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,

$$\nabla_1^2\Psi + \nabla_2^2\Psi + \frac{8\pi^2 m}{h^2}\left\{E - \left(\frac{e^2}{R} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}\right)\right\}\Psi = 0,$$

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 interaction of the present charge distribution,"[8] and that this integral could be solved analytically as a function of the internuclear distance, R. In contrast, E_{12} did not permit such a simple, classical interpretation as E_{11} did. Moreover, it was difficult to calculate all the integrals involved in E_{12}, particularly the one known as the exchange integral, $\int \frac{\Psi_1\varphi_2\Psi_2\varphi_1}{r_{12}}d\tau$. Heitler and London circumvented this difficulty by considering only its upper limit, and drew approximate graphs of E_α and E_β. (see Fig. ??)

According to this energy diagram, E_β represented a repulsion between the atoms at any internuclear distance; E_α showed an attraction at a larger distance and a repulsion at a smaller distance, having a minimum value when the internuclear distance R was 1.5
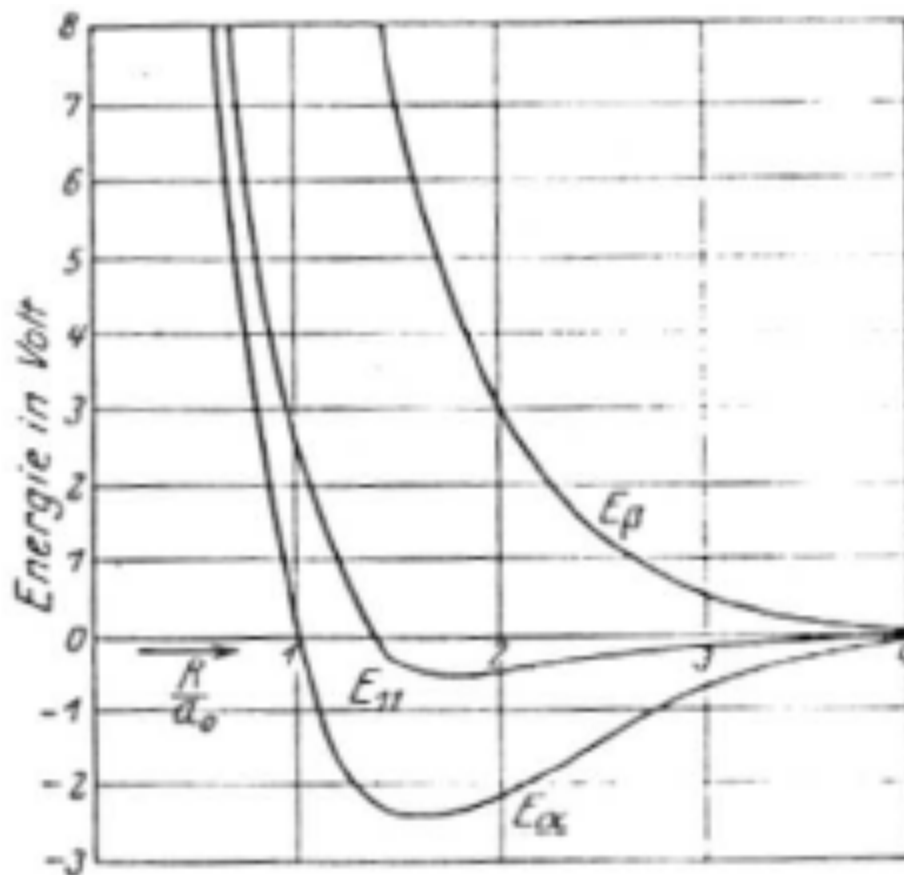
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[8]Heitler and London, "Wechselwirkung," 461.

Figure 1.1: Heitler and London's energy diagram of the hydrogen molecule. E_α represents nonpolar attraction; E_β elastic reflection; and E_{11} coulomb interaction.

a_0 or 0.8 Å. From the graph of E_α, the corresponding dissociation energy or the binding energy was about 2.4 eV.[9]

Heitler and London did not compare their theoretical values with observed ones, presumably because the agreement was not particularly good for the binding energy. 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 *non-polar* hydrogen atoms without considering perturbation by polarization. This was due to the 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).[10]

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[9]Kostas Gavroglu and Ana 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, "Quantum Chemistry," p. 63; and Gavroglu, *Fritz London*, p. 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.

[10]Heitler and London, "Wechselwirkung," pp. 460–63.

What was the nature of this exchange effect? Why did non-polar 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, $\frac{E_\beta - E_\alpha}{h}$. But they found it difficult to characterize this effect in the language of classical mechanics. At least, they saw the exchange effect as "closely related with the quantum mechanical resonance phenomenon" introduced by Werner Heisenberg a year earlier for the problem of helium,[11] in that both resonance and exchange originated from the indistinguishability of electrons. 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."[12]

The interpretation of E_α and E_β was important in another way. The Pauli exclusion principle required E_α to be an energy state in which the electrons were in opposite spin orientations (antiparallel); and E_β, in the same orientation (parallel). Therefore, the electronic spin state was a useful indicator of the molecular formation: the antiparallel spin state led to the attraction (thus, bonding), while the parallel one corresponded to the unstable excited state. In other words, the chemical bond resulted from the pairing of electrons of different spin orientations, and valence was predicated on this pairing. This established a connection between the spin theory of valence and the Lewis theory of paired-electron bond which London elaborated in his papers of 1928.[13]

Toward Better Agreement between Theory and Experiment

The further development of Heitler and London's treatment of the hydrogen molecule went in two directions. On the one hand, two Americans, John C. 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.[14] On the other hand, there were those who attempted to make the Heitler and London approach acceptable quantitatively as well as qualitatively. They calculated the exchange integral, employed physical and chemical insights to narrow the gap between theory and experiment, and even developed different kinds of computational schemes.

The first step in this direction was made by Yoshikatsu Sugiura, who came from

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[11]Werner Heisenberg, "Mehrkörperproblem und Resonanz in der Quantenmechanik," *Zeitschrift für Physik*, **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," *Studies in History and Philosophy of Modern Physics* **27** (1996), 23–45; 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. 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), pp. 282–301.

[12]Heitler and London, "Wechselwirkung," p. 461. For Heitler and London's concern about (mis)interpretation of exchange effect, see Gavroglu and Simoes, "Quantum Chemistry," pp. 61–5.

[13]Heitler and London, "Wechselwirkung," pp. 465–8. Fritz London, "Zur Quantentheorie der homöopolaren Valenzzahlen," *Zeitschrift für Physik*, **46** (1928), 455–77; and idem, "Zur Quantenmechanik der homöopolaren Valenzchemie," *Zeitschrift für Physik*, **50** (1928), 25–51.

[14]Buhm Soon Park, "The Contexts of Simultaneous Discovery: Slater, Pauling, and the Origins of Hybridisation," *Studies in the History and Philosophy of Modern Physics*, **31** (2000), 451–474.

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.[15]
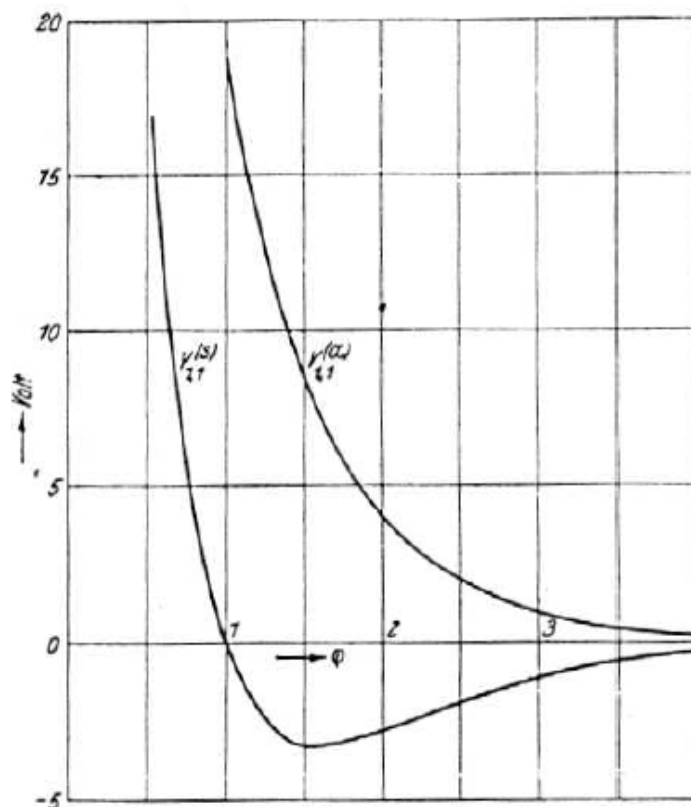

Figure 1.2: Sugiura's energy diagram for the hydrogen molecule: Sugiura's notations of $V_{1,1}^{(s)}$ and $V_{1,1}^{(a)}$ correspond to Heitler and London's E_{11} and E_{12}.

Sugiura showed that the equilibrium separation of H2 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 empirical value, 4.4 eV, than Heitler and London's had been. The agreement was, in his opinion, satisfactory.

Shou Chin Wang, a Chinese physicist studying at the University of Columbia for his doctoral degree, was one of those interested in the problem of the hydrogen molecule. Although his thesis adviser was an old-fashioned mathematical physicist, Wang had a chance to learn quantum mechanics by reading the latest issues of *Zeitschrift für Physik* in a study group led by Ralph Kronig.[16] Wang's approach was basically the same as

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[15]Yoshikatsu Sugiura, "Über die Eigenschaften des Wasserstoffmoleküls im Grundzustande," *Zeitschrift für Physik*, **45** (1927), 484–92. On Born's guidance, see ibid., p. 492.

[16]Katherine R. Sopka, *Quantum Physics in America*, 1920–1935 (New York: Arno Press, 1980), pp.

Heitler and London's in that he formed a linear combination of wave functions assuming atomic individuality in the molecule.[17] However, Wang attacked the problem with a different mathematical technique. Instead of calculating the perturbation energy, he adopted what had been known as the Ritz method or the variation method, in which one could determine the coefficients of the linear combination in a way that gave the lowest possible energy value. This method had been successfully applied to the problem of helium by the German physicist Georg W. Kellner.[18] In addition, Wang was also attracted to Kellner's use of the effective nuclear charge Ze as a variable parameter, which took into account the screening effect of electrons over nuclei—the effect that the electronic orbits are contracted into a smaller region because of the Coulombic attraction between electrons and nuclei. Putting the effective nuclear charge into the hydrogen eigenfunctions, Wang finally obtained improved results: the equilibrium separation was 0.73 Åand the dissociation energy 3.76 eV. When he had almost completed his paper, Wang received the latest issue of *Zeitschrift für Physik* containing Sugiura's paper. Nevertheless, Wang was confident that his work was worthy of publication for the reason that he "used a new method of calculation and arrived at some results in a little better agreement with the experimental data than Sugiura's."[19]

Sugiura and Wang did not attempt to make further improvements of their calculations.[20] But the persistent discrepancy between theory and experiment continued to attract attention from young scientists like Nathan Rosen. Rosen was to be best known later as one of the co-authors 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."[21] He maintained that there should be a better way to inquire as to the various complicated interactions between atoms, such as the distortion of the charge distribution. Rosen valued Wang's treatment of this distortion

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3.48–3.50, and p. 3.102.

[17] Shou C. Wang, "The Problem of the Normal Hydrogen Molecule in the New Quantum Mechanics," *Physical Review*, **31** (1928), 579–86.

[18] Georg W. Kellner, "Die Ionisierungsspannung des Heliums nach der Schrödingerschen Theorie," *Zeitschrift für Physik*, **44** (1927), 91–112.

[19] Wang, "Hydrogen Molecule," p. 579.

[20] After his research trip in Europe, Sugiura returned to Tokyo to join the Institute of Physical and Chemical Research (Riken), which had been established in 1917, modeled after Germany's Imperial Institute for Physics (Physikalisch-Technische Reichsanstalt). Along with Bunsaku Arikatsu and Woshio Nishina, Sugiura also lectured on quantum mechanics at Kyoto from 1929 to 1931, spreading the "Copenhagen spirit." Among his students were the future Nobel laureates, Hideki Yukawa and Shinichiro Tomonaga. See Hideki Yukawa, *Tabibito*, trans. L. M. Brown and R. Yoshida (Singapore: World Scientific, 1982), pp. 176–7. For the context for the establishment of Riken, see Itakura Kiyonobu and Yagi Eri, "The Japanese Research System and the Establishment of the Institute of Physical and Chemical Research," in *Science and Society in Modern Japan*, ed. Nakayama Shigeru, David L. Swain, and Yagi Eri (Cambridge: MIT Press, 1974), pp. 158–201. 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 own country, China, to teach modern physics at the University of Chekiang and later at Peking University. For Wang's professional career, see National Research Council, *National Research Fellowships*, 1929–1944 (Washington, D.C.: National Research Council, 1944), p. 37.

[21] Nathan Rosen, "The Normal State of the Hydrogen Molecule," *Physical Review*, **38** (1931), 2099–114, quote on 2099.

with the altered atomic radius; but to him, it was "rather far from the goal." 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 had been known that one of the weaknesses in the Heitler and London approach was its neglect of the possibility of ionic configurations in molecules. Sidney Weinbaum examined this problem under the guidance of Pauling at the California Institute of Technology (Caltech). He added ionic terms to wave functions originally proposed by Heitler and London, finding an improvement in the binding energy of 0.0031 eV or 3 percent over Sugiura's value.[22] He also showed that the consideration of the effective nuclear charge plus the ionic term would yield an improvement of 8 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 ones obtained by Heitler and London's method.

In 1933, Hubert M. James and Albert S. Coolidge obtained by far the most accurate theoretical value, using the coordinate of the interelectronic distance, the method developed by the Norwegian physicist Egil Hylleraas for helium.[23] James and Coolidge were at Harvard University: James as a physics graduate student working toward his doctoral degree, and Coolidge as a chemistry professor. Though from different departments, they had a common background in that both learned quantum mechanics in Edwin C. Kemble's lectures. 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).[24] During his calculations, James found that Cl_2 was too complex to be handled by the Heitler and London method, and thus changed his problem to a much simpler one, that of 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."[25]

James and Coolidge abandoned the fundamental assumption of the Heitler and London method, i.e., the atomic individuality. Instead of approximating the molecular wave function with the atomic eigenfunctions, they started with a trial function having many

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[22]Sydney Weinbaum, "The Normal State of the Hydrogen Molecule," *Journal of Chemical Physics*, **1** (1933), 593–6.

[23]Hubert M. James and Albert S. Coolidge, "The Ground State of the Hydrogen Molecule," *Journal of Chemical Physics*, **1** (1933), 825–35.

[24]In fact, Hubert M. 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 James to Spencer R. Weart, May 1980, American Institute of Physics Early 1930s Ph.D. Project, "Hubert James," MB 31484.

[25]James to Sopka, 9 May 1972, quoted in Sopka, *Quantum Physics*, pp. 4.87–4.88.

variable parameters:

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

where λ_1, λ_2, λ_3, and λ_4 were four elliptic coordinates of the following relations,

$$\lambda_1 = \frac{r_{1a} + r_{1b}}{R}$$

$$\lambda_2 = \frac{r_{2a} + r_{2b}}{R}$$

$$\mu_1 = \frac{r_{1a} - r_{1b}}{R}$$

$$\mu_2 = \frac{r_{2a} - r_{2b}}{R}$$

and the fifth coordinate, $\rho = \frac{2r_{12}}{R}$, had the interelectronic distance in it. The summation was to extend over the positive or zero values of the indices, with the restriction that $j+k$ must be even, which was required by nuclear symmetry. The function was also able to take 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 1.4 a_0 (or 0.74 Å), and the exponent (δ) at 0.75 a_0, and then solved a set of equations which came from the condition of making values of the C's 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, the improvement slowed. The computations became more and more laborious, because the incorporation of each new term required the computation of numerous integral terms. The success of James and Coolidge's treatment was immediately recognized as a "thoroughly satisfactory treatment of the normal hydrogen molecule, the only improvement which we may look forward to being the increase in accuracy by the inclusion of further terms."[26] And their paper was also praised as showing that Schrödinger's equation was reliable for molecules as well as atoms. Charles A. Coulson later said, "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."[27]

James and Coolidge's success was a source of optimism that molecular properties could be computed with only the Schrödinger equation and several fundamental constants, such as the electronic charge (e), the electronic mass (m_e), Planck's constant (h), the atomic number (Z), and the masses of the nuclei involved, with no further empirical data. In another sense, however, James and Coolidge's success was a source of pessimism: the amount of computation was simply formidable. Thus textbook writers of quantum chemistry noted:

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[26] Pauling and Wilson, *Quantum Mechanics*, p. 351.

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

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 (Wang, 1928)	3.76	0.73
Heitler-London with screening + polarization term (Rosen, 1931)	4.02	0.74
Heitler-London + ionic term (Weinbaum, 1933)	3.21	0.90
Heitler-London with screening + ionic term (Weinbaum, 1933)	4.00	0.74
Heitler-London with screening + polarization term + 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

Table 1.1: Quantum-mechanical calculations of the binding energy and equilibrium separation of the hydrogen molecule from 1927 to 1933. Source: John H. Van Vleck and Albert Sherman, "The Quantum Theory of Valence," *Reviews of Modern Physics*, **7** (1935), 167–228. The molecular orbital approximation performed poorly even with the consideration of the screening effect. See Charles A. Coulson, *Valence* (Oxford: Clarendon Press, 1952), p. 119.

> However, the labor involved in these calculations is so great even for these simple systems [like 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.[28]

As James found, "a good fortune" of unjustified approximations could provide remarkably good results for diatomic molecules, such as Li_2, LiH, Na_2, K_2, and KH.[29] One of the often used assumptions 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. Neglect of the inner-shell electrons gave a nice

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[28] 28 Henry Eyring, John Walter, and George E. Kimball, *Quantum Chemistry* (New York: John Wiley & Sons, 1944), p. 217.

[29] Hubert M. James, "Wave-Mechanical Treatment of the Li2 Molecule," *Journal of Chemical Physics*, **2** (1934), 794–810; and idem, "Wave-Mechanical Treatment of the Molecule Li_2^+," *Journal of Chemical Physics*, **3** (1935), 9–14. See also John H. Van Vleck and Albert Sherman, "The Quantum Theory of Valence," *Reviews of Modern Physics*, **7** (1935), 167–228, esp. 185–6.

agreement between the calculated and observed values of the binding energy of Li_2, but James showed that the consideration of inner-shell electrons would completely destroy the agreement. The rigorous treatment gave poorer results than the rough one! It was called "the nightmare of inner shells."[30] In fact, James proposed a remedy for this problem: describe valence electrons with the same function as he and Coolidge had devised for hydrogen, and treat non-valence electrons by means of simple atomic orbitals. However, 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."[31]

James and Coolidge continued their collaboration until 1940, working on polyatomic molecules, but with no notable success.[32] Their research program demanded intensive labor with the then available computing facilities. It was only after the war that human patience was greatly relieved by the development of electronic digital computers[33]; and the field of rigorous computations of molecular properties was then opened up again. But James and Coolidge, like other workers involved in the H2 problem, never returned to the field. Paradoxically, James and Coolidge's work heralded the coming of the "dark ages" of the *ab initio* method.[34]

From Helium to Many-Electron Atoms

The point of departure for the problem of many-electron atoms was, as always, the normal helium atom: various approximation methods were first developed and tested for helium before being applied to larger atoms. The criteria for testing a method, in view of its further applicability, included the amount of labor in computations as well as the degree of accuracy of computed results. The desideratum was that approximations would make problems "manageable" without the expense of accuracy; but that was difficult to achieve.

By 1930, an outstanding agreement between theory and experiment on the helium

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[30] Van Vleck and Sherman, "Quantum Theory of Valence," pp. 185–6.

[31] Ibid., pp. 186–90, quote on p. 190. This part of the review article was written by James. See footnote 37.

[32] James to Weart, May 1980, American Institute of Physics Early 1930s Ph.D. Project, "Hubert James," MB 31484. In 1940, James became an assistant professor at Purdue University, where his interests were diverted to polymer and solid-state physics.

[33] 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), pp. 219–247.

[34] Schaffer, Ab Initio *Methods*, p. 4. Indeed the quantitative investigation of molecules, being limited to relatively simple ones, languished in the late 1930s and 40s. Only a small number (seven) of studies on the hydrogen molecule 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," *Reviews of Modern Physics*, **32** (1960), 211–8. Andrea I. Woody also points out the difficulty of applying James and Coolidge's method to other molecules, and sketches the development of the Configuration Interaction method after the war. Andrea I. Woody, "Early Twentieth Century Theories of Chemical Bonding: Explanation, Representation, and Theory Development (Quantum Chemistry)" (Ph.D. Diss., University of Pittsburgh, 1997).

problem had been achieved by Egil A. Hylleraas.[35] Hylleraas took his Ph.D. at the University of Oslo in 1924, working on the crystal lattice theory. Two years later, after spending the intervening period as a school teacher, he joined Born's group at Göttingen on a Fellowship of 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.[36] At that time, the basic understanding of the spectral properties of helium had been well established by Heisenberg; but there was still a broad gap between the spectroscopic measurement 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, as given by Albrecht Unsöld (20 eV).[37] The introduction of an effective nuclear charge by Geroge Kellner reduced the discrepancy from about 4 to 1.5 eV,[38] which was still a significant amount. Under Born's guidance, Hylleraas began to attack the problem of helium with a noisy electric desk calculator called the Mercedes Euclid to handle a large volume of numerical work. Using a trial 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. It was soon "greatly admired and thought of as almost a proof of the validity of wave mechanics, also, in the strict numerical sense."[39] Not fully satisfied with this result, however, Hylleraas continued to work on reducing the discrepancy after his return to Oslo. Finally, he made a major advance by introducing in the wave function a new coordinate of the interelectronic distance, $u = \frac{r_{12}}{a_0}$, which occurred in the interaction term for the two electrons. The final theoretical value for the energy of the helium atom was only 0.0016 eV below the experimental value: a discrepancy like this could be attributed to a numerical error in the calculations or to experimental error or possibly to some small effects such as electron-spin interactions, motion of the nucleus, and so on.[40] It was seen as a triumph for quantum mechanics when 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."[41]

And yet it was not easy to adapt Hylleraas's method to heavy atoms, because the number of terms that had to be computed increased very rapidly with increasing numbers of electrons. Even in the early 1960s, no successful application of the method was reported for atoms heavier than lithium, a three-electron system.[42] However, the intro-

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[35] Egil A. Hylleraas, "Über den Grundzustand des Heliumatoms," *Zeitschrift für Physik* **48** (1928): 469–94; idem, "Neue Berechnung der Energie des Heliums in Grundzustande, sowie des tiesfsten Terms von Orthohelium," *Zeitschrift für Physik*, **54** (1929), 347–66; and idem, "Über den Grundterm der Zweielektronenprobleme von H^-, He, Li^+, Be^{++} usw.," *Zeitschrift für Physik*, **65** (1930), 209–225.

[36] For Hylleraas's educational background and Born's influence upon him, see Egil A. Hylleraas, "Reminiscences from Early Quantum Mechanics of Two-Electron Atoms," *Reviews of Modern Physics*, **35** (1963), 421–31.

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

[38] Kellner, "Ionisiderungsspannung des Heliums," pp. 91–112.

[39] Hylleraas, "Grundzustand des Heliumatoms," pp. 469–94. The quote is from Hylleraas, "Reminiscences," p. 427.

[40] Linus Pauling and E. Bright Wilson, *Introduction to Quantum Mechanics With Applications to Chemistry* (New York: McGraw-Hill Book Company, 1935), p. 224.

[41] Ibid., pp. 222–4.

[42] John C. Slater, "The Electronic Structure of Atoms—The Hartree-Fock Method and Correlation," *Reviews of Modern Physics*, **35** (1963), 484–7.

duction of r_{12} was not the only method for considering the inter-electronic interaction known as *electronic correlation*. Hylleraas was also a pioneer of another method called the *configuration interaction*. Instead of approximating the "true" wave function with one-electron functions, he devised a way of using a set of functions of any number, possibly an infinite number.[43] But the computational difficulty with this method, along with the modest result, discouraged him from proceeding further.

Less accurate but more applicable than Hylleraas's two methods was the use of wave functions of the simple, analytic form which might relieve the labor of computations. The hydrogen eigenfunctions—the solutions of the Schrödinger equation for the hydrogen problem—were such functions; and, in fact, they were exact solutions for other atomic problems when the interaction between the electrons was entirely neglected. Kellner partially took care of this interaction in helium, by putting an effective nuclear charge into the function and fixing its value with the variation principle. This technique was soon applied to lithium and the other elements in the first row of the periodic table,[44] where, instead of the original wave functions of hydrogen, their asymptotic form (a form at large distances between a nucleus and electrons) was used. The modified wave functions had the same angular part as the hydrogen counterparts had, but their radial part, $r^{n^*-1} e^{-\left[\frac{(Z-s)r}{n^*}\right]}$, was different in that it had no radial nodes. Here r was the distance between nucleus and electron, n^* the effective quantum number (the parameter for the principle quantum number), Z the nuclear charge, and s the screening constant. In 1930 Slater used this form of wave function to discuss the size, the ionization potential, and magnetic properties of much heavier atoms like Fe and Co. Hence the name the Slater-Type Orbitals (STOs). Yet Slater did not determine the screening constants and other parameters with the variation principle, but adjusted them using empirical values. His was the semi-empirical study of atomic properties. Slater thus said: "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."[45]

Another approach was developed by the Englishman Douglas R. Hartree in 1928, called the Self-Consistent-Field (SCF) method. 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 analytical functions. Hartree was a Cambridge man, who was born and educated, taught, and died in Cambridge.[46] He excelled in mathematics at St. John's College, Cambridge, graduating in 1921 with First Class Honors in Part I of the Mathematical Tripos and Second Class Honors in Part

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[43] Egil A. Hylleraas, "Über den Grundzustand des Heliumatoms," *Zeitschrift für Physik*, **48** (1928), 469–94.

[44] Victor Guillemin, Jr. and Clarence Zener, "Über eine einfache Eigenfunktion für den Grundzustand des Li-Atoms und der Ionen mit drei Elektronen," *Zeitschrift für Physik*, **61** (1930), 199–205; and Clarence Zener, "Analytic Atomic Wave Functions," *Physical Review*, **36** (1930), 51–6.

[45] John C. Slater, "Atomic Shielding Constants," *Physical Review*, **36** (1930), 57–64, quote on p. 57.

[46] C. G. Darwin, "Douglas Rayner Hartree," *Biographical Memoirs of the Fellows of the Royal Society*, **4** (1958), 103–16; and R. B. Lindsay, "Douglas Rayner Hartree," in *Dictionary of Scientific Biography*, vol. 6, ed. Charles C. Gillispie (New York: Charles Scribner's Sons, 1970), pp. 147–8. See also Ana Simões and Kostas Gavroglu, "Quantum Chemistry in Great Britain: Developing a Mathematical Framework for Quantum Chemistry," *Studies in the History and Philosophy of Modern Physics*, **31** (2000), 511–48.

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 the 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 course of time along it, 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."[47]

As Hartree set out in the introduction, this paper contained a 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.[48]

His logic was clear: (1) assume a simple type of field (here, a central field, i.e., a function of the distance r from the nucleus only); (2) impose quantum conditions on this field; (3) express the effective nuclear charge Z as a function of r, and solve the integral for the field, V $\left(V = \int_r^\infty \frac{Z}{r^2}\, dr\right)$; (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 only from the theory. 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 a 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.[49] Moreover, his study indicated a notable paradox of the Bohr theory: the electrons moving *in sharply defined orbits* produced a *smooth charge distribution curve*, which went quite a long way outside the boundary of the atom.[50] This was explained only after the arrival of quantum mechanics.

Hartree was awarded his Ph.D. 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

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[47]Douglas R. Hartree, "On Some Approximate Numerical Applications of Bohr's Theory of Spectra," *Proceedings of the Cambridge Philosophical Society*, **21** (1923), 625–41.

[48]48 Ibid., p. 625.

[49]Hartree acknowledged that E. Fues did similar calculations independently, but argued that his own method was more general than Fues' was. See Ibid. 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), p. 53.

[50]Hartree, "Numerical Applications," p. 639. See also Slater, "Structure of Atoms," p. 485.

Figure 1.3: Hartree's early idea of the Self-Consistent-Field 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, $\frac{r}{a}$, 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).

at the University of Manchester in 1929. It was in this postdoctoral period that Hartree developed a quantum-mechanical method of investigating the electronic structure of atoms.[51]

The overall structure of Hartree's new method looked similar to that of his old one.[52] First of all, Hartree started by assuming a central field (of the 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 and this charge distribution, the "final field."

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

[52] "Wave Mechanics. Part II," pp. 111–4.

He summarized the procedure with the following diagram for a core electron:

<div align="center">

Initial Field

↓

Initial Field corrected for each core electron

↓

Solutions of Wave-Equation for core electrons

↓

Distribution of Charge

↓

Final Field

</div>

If the final field was the same as the initial field, the field would be called "self-consistent"; and no more numerical work would be necessary. If not, one should repeat the same procedure by using 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 non-empirical, *ab initio*. This feature was the major difference between the SCF method and his previous one. As an example, Hartree showed how successive approximations narrowed the difference between the effective nuclear charge of initial and final field for rubidium (Rb), an atom having thirty-seven electrons.[53]
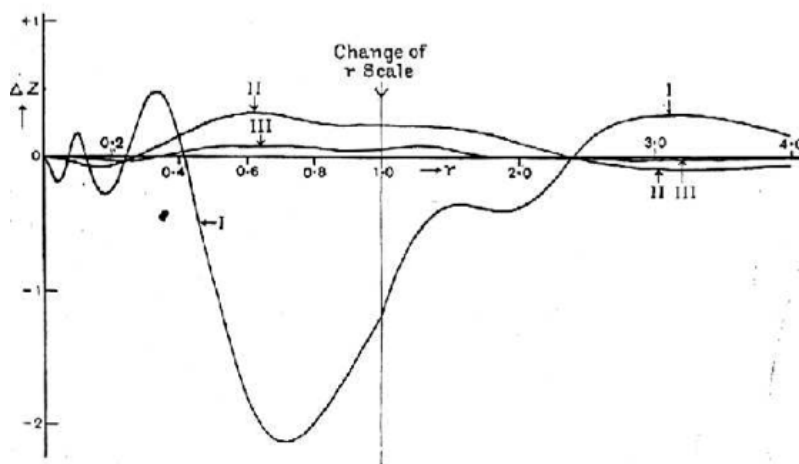

Figure 1.4: Hartree's three approximations to Self-Consistent-Field for Rb. Difference ΔZ between effective nuclear charge of initial and final field was plotted against r for the three approximations (Curves I, II, and III).

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, within the difference of 0.2 eV from the observed

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[53]Ibid., pp. 117–8.

value. He regarded this "very close agreement" as an "empirical justification of the simple approximations," if not a "notable success of the method."[54] Convinced of the usefulness of his approximation method, Hartree remarked:

> It is thought that the distribution of charge in the self-consistent field is probably the best approximation to the actual distribution of charge in the atom which can be obtained without very much more elaborate theoretical and numerical work, and so is the most suitable to use in any problems involving this distribution of charge; also it is hoped 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.[55]

Hartree's Self-Consistent-Field Method and Slater's Determinantal Method

Only a few months after the publication of Hartree's papers in 1928, J. A. Gaunt of Trinity College offered a critical review of his SCF method.[56] Gaunt's purpose was not to disprove the method, but to assess Hartree's assumptions in the light of recent developments of quantum mechanics. He saw the assumptions as "simple and picturesque," and "open to several objections" from a rigorous point of view. He particularly 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 doubt seriously; Hartree did not even consider the Pauli exclusion principle, the spin state of electrons, or Heisenberg's resonance phenomenon, in dealing with many-electron systems. Hartree's method was flawed in this regard. Investigating the error possibly caused by the neglect of resonance terms, however, Gaunt showed that the terms responsible for 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 C. Slater of Harvard University.[57] Like Gaunt, Slater stressed that Hartree should have considered the resonance interactions between electrons in his approximation. In addition, Slater pointed out, Hartree also neglected the fact 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 of s orbit (where the azimuthal quantum number $l = 0$) the electron's own contribution to the field was not centrally 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."[58] Besides, Slater found an inconsistency in Hartree's

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[54] Ibid., p. 117.

[55] Ibid., p. 114.

[56] J. A. Gaunt, "A Theory of Hartree's Atomic Fields," *Proceedings of the Cambridge Philosophical Society*, **24** (1928), 328–42.

[57] John C. Slater, "The Self Consistent Field and the Structure of Atoms," *Physical Review*, **32** (1928), 339–48.

[58] Hartree, "Wave Mechanics. Part II," p. 112.

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.[59]

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 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."[60] 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, I would be glad to send you any numerical data I possess."[61]

Slater gave a critical review of the SCF method in 1928, when his main interest moved from the radiation problem to the theory of matter—atoms, molecules, and metals.[62] Slater sought to find out the proper ways of incorporating Pauli's exclusion principle into the problem of many-electron atoms, as Heisenberg had done for helium with the concept of resonance. In fact, many competent theoretical physicists, such as Eugene Wigner, Frederick Hund, Herman Weyl, and Walter Heitler, had been engaged in this problem since the publication of Heisenberg's helium paper in 1926. They followed the procedure Heisenberg had prescribed: first, they tried to find the appropriate form of wave functions of the ordinary position coordinates (x, y, z), and then considered the spin needed to make the whole wave function antisymmetric with respect to the change of electrons. To this end, they used group theory. In contrast, Slater took the opposite tack, by 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, than by group theory.[63]

In the development of the determinantal method, Slater owed much to Hartree. For

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[59]Slater, "Self Consistent Field," pp. 346–8.

[60]Ibid., p. 348.

[61]Hartree to Slater, 6 July 1928, D. R. Hartree, #1, John C. Slater Papers, American Philosophical Society, Philadelphia.

[62]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 moved 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. Paul A. M. Dirac, "The Quantum Theory of the Emission and Absorption of Radiation," *Proceedings of the Royal Society*, **A114** (1927): 243–65. Slater later wrote that after reading Dirac's paper, "It was obvious that I would never catch up with Dirac to the point of being clearly ahead of him. Thus at this point I shifted my interest to the helium atom." Quoted in Silvan S. Schweber, "The Young John Clarke Slater and the Development of Quantum Chemistry," *Historical Studies in the Physical and Biological Sciences* **20** (1990): 339–406, at p. 373. In footnote 94, Schweber has pointed out that Slater tried again and again but in vain to unify the quantum theory of radiation with that of matter.

[63]John C. Slater, "The Theory of Complex Spectra," *Physical Review* **34** (1929): 1293–322.

Slater profited from the analysis of Hartree's papers, from which he learned that the assumption of the central field in many-electron atoms worked out well, and that the one-electron approximation might be a good starting point even if resonance was neglected. Therefore, Slater adopted the assumption of the central field, with a slight modification for simplicity in 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."[64] Slater then used the one-electron approximation, representing each electron's wave function with both the position and spin coordinates. As Slater acknowledged, the process of building up the antisymmetric wave function with a determinant was well known.[65] 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 "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 liked it. "No other work I have done," Slater wrote in his autobiography, "was so universally popular."[66] This paper was particularly welcomed by those physicists who saw group theory as an arcane, incomprehensible mathematical manipulation: Slater later heard such remarks as "Slater had slain the 'Gruppenpest' [the pest of group theory]." He met Hartree at a conference in Zurich, before going to Leipzig to spend half a year with Heisenberg and Hund.

While in Leipzig, Slater found that Hartree's Self-Consistent-Field method was not well received among the quantum theorists. Despite some theoretical justifications made 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.[67] This time he insisted upon its close relation to the procedure a scientist should take when applying the variation principle to the simple product of one-electron wave functions. He said:

> 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

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[64] Ibid., 1299.

[65] Ibid., 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," *Proceedings of the Royal Society* **A124** (1929): 119–42.

[66] Slater, *Solid-State and Molecular Theory*, 62–3. Slater noted the responses from Hund, Waller, Hartree, Bloch, Heisenberg, and Wigner. See also Schweber, "John Clarke Slater," 377.

[67] John C. Slater, "Note on Hartree's Method," *Physical Review* **35** (1930): 210–1.

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.[68]

The variation 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 of them. Slater realized that this way of finding the "best" approximate wave function was tantamount to that of 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 variation 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 variation procedure, the comparison was made as to 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 there how to set up an elaborate formulation of applying the variation principle to the antisymmetric function. A few months later, the Russian physicist Vladmir Fock developed another way of formulating the SCF method with the variation principle. Unfamiliar with Slater's determinantal method, Fock used the technique of the permutation group.[69] Hence the Hartree-Fock (instead of the Hartree-Slater-Fock) method. In 1935, finally, Hartree simplified Fock's formulation with Slater's determinantal method.[70]

The Hartree-Fock method was universally accepted, not because it produced results as accurate as 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 1 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 antisymmetricity 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 made to consider electron correlation in a more general way.[71] Despite this problem, there was a consensus that Hartree-Fock ap-

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[68]Ibid., 211.

[69]Vladmir Fock, "Näherungsmethode zur Lösung des quantenmechanischen Mehrkörperproblems," *Zeitschrift für Physik* **61** (1930): 126–48. This paper was received on 21 February 1930. In it, Fock did not mention any of Slater's work; but he cited Gaunt's paper on Hartree's method.

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

[71]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, "Hartree-Fock Method," 480.

proximations 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."[72]

Although the idea of the self-consistent-field was the central part of 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 of the electrons in atoms, he had to solve the differential equation of radial function, 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, the distance from the nucleus; and computations took up so much of his energy that he failed to keep abreast of the recent development of quantum theory. In reply to Slater's criticism in 1928, he said: "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."[73] In the 1930s Hartree was fortunate to have the assistance of his father, William Hartree, who liked doing the computing work as an occupation for his retirement.[74] Hartree also looked for computing machines to relieve the amount of human labor. In the early 1930s, he visited MIT to learn about Vannevar Bush's differential analyzer[75]; and on his return to Britain, he set up his own model of a differential analyzer with Meccano parts (children's toys) to demonstrate its working. After World War II, he again made a trip to America to become familiar 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 lent his expertise to the installation of digital computers in England, including the EDSAC (Electronic Discrete Variable Automatic Computer) in Cambridge and the Ferranti in Manchester. The popularization of computers and their application to scientific problems became his major activity for several years after his return to Cambridge in 1946, when he succeeded 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."[76]

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[72]Eyring et al., *Quantum Chemistry*, 166.

[73]Hartree to Slater, 6 July 1928, D. R. Hartree #1, John C. Slater Papers, American Philosophical Society, Philadelphia.

[74]In 1939, Hartree wrote to Slater: "As you may know, all the computing work in the calculations of atomic structures which my father and I have published during the last several years has been done by him. He likes it as an occupation for his retirement, and I am glad to have his help, as I would not have the time to carry through the rather extensive computations myself." Hartree to Slater, 1 November 1939, D. R. Hartree, #1, John C. Slater Papers, American Philosophical Society, Philadelphia.

[75]Perhaps it was Slater who provoked Hartree to pay a visit to MIT. In his letter to Hartree on 25 November 1931, Slater gave a description of Bush's differential analyzer, and said he planned to use this machine in the SCF calculations. D. R. Hartree, #1, John C. Slater Papers, American Philosophical Society, Philadelphia.

[76]Douglas R. Hartree, *Calculating Machines, Recent and Prospective Developments* (Cambridge: Cambridge University Press, 1947). Thirteen out of forty publications by Hartree after 1946 were intended to inform the readers of various journals and governmental officials about calculating machines. For the bibliography of Hartree's work, see C. G. Darwin, "Douglas Rayner Hartree," pp. 112–6. For

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Hartree's deep interest in improving calculation techniques and easing human labor did not earn him much respect among quantum physicists. Slater found it unfair. He said: "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."[77] 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.[78]

Yet Hartree was not alone in having to cope with the prejudice against computation-oriented research. Sugiura's work failed to impress even Heitler, who said: "It appears that there are in the world some hard working dwarfs" said Heitler, who put more value on gaining physical explanations than having exact computations.[79] 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."[80]

To a large extent, the historical significance of computation in quantum mechanics has been undervalued or unexplored. How much, then, do we have to 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 may be in the "practice" of theory to make its incremental improvement or circumvent technological or even conceptual constraints. In this respect, the following two recollections are illustrative. Heitler recalled his Eureka moment:

> 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

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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," *Annals of the History of Computing*, **14** (1992), 10–15; Paul A. Medwick, "Douglas Hartree and Early Computations in Quantum Mechanics," *Annals of the History of Computing*, **10** (1988), 105–11.

[77]Slater, *Solid-State and Molecular Theory*, p. 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." He 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., p. 42.

[78]Clemens C. J. Roothaan, "New Developments in Molecular Orbital Theory." *Reviews of Modern Physics*, **23** (1951), 61–89.

[79]Quoted in Gavroglu, *Fritz London*, p. 47.

[80]Werner Heisenberg to Pascual Jordan, 28 July 1926, quoted in Mehra and Rechenberg, *The Formulation of Matrix Mechanics and Its Modifications*, p. 301.

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.[81]

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, although, 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 said:

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.[82]

Working with machines that seem primitive from today's standpoint (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."[83] James's Eureka moment came with the realization that enormous labor would be required to proceed his idea, and his rewarding moment came when the theoretical values came closer to experimental ones.

Shortly after the advent of quantum mechanics, several ways of solving the many-electron Schrödinger equation were developed, but there were considerable difficulties in carrying out these solutions. 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."[84] Sugiura, James, Hartree, and other *ab initioists* were those who did it. To them, making a theory really work in atomic and molecular

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[81] Walter Heitler, AHQP (Archive for the History of Quantum Physics) Interview, pp. 541–542, Historical Development of Quantum Theory, volume 6. 1963.

[82] James to Sopka, 9 May 1972, quoted in Sopka, *Quantum Physics*, pp. 4.87–4.88.

[83] Ibid., p. 4.88.

[84] Per-Olov Löwdin, "Recent Simplifications in the Molecular Orbital Theory of Calculating Energy Levels," in *Proceedings of the International Conference of Theoretical Physics* (Tokyo: Nippon Bunka Insatusha Co., 1953), 599–609, quote on 599.

problems was as important as developing it 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.