



The Contexts of Simultaneous Discovery: Slater, Pauling, and the Origins of Hybridisation

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1. Introduction

Simultaneous discovery in science has been a subject of close historical investigations, not only for assessing claims of priority, which occasionally generate controversy rather than consensus, but also for understanding the cultural and intellectual context of the time. Thomas S. Kuhn is a pioneer in the contextual study of simultaneous discovery, and his paper on the formulation of the first law of thermodynamics has already become a classic.¹ But it should be noted that Kuhn's use of 'context' is two-fold; and that he seeks to qualify the meaning of 'simultaneous discovery'. In the first place, he is puzzled by the diversity of discovery: he has examined a dozen scientists, whose papers have only fragmentary resemblance with no two seeming to say the same thing. For him, the experimental and conceptual elements of the law of energy conservation emerged in a disorderly way across various disciplinary contexts and individual circumstances, in which the workers had different goals and approaches. In the second place, the fact that these elements became suddenly accessible and recognisable between 1830 and 1850 leads Kuhn to look for the broad, common context, such as the availability of conversion processes, the concern with

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¹ Kuhn (1969). I use the following abbreviations: 'JSP' = John C. Slater Papers, American Philosophical Society Library, Philadelphia; 'LPP' = Linus Pauling Papers, Oregon State University, Corvallis.

engines, and *Naturphilosophie*. The interweaving of the individual, disciplinary context with the broad, interdisciplinary one characterises Kuhn's understanding of simultaneous discovery.

This paper investigates a well-known case of simultaneous discovery in twentieth-century chemistry, the origins of the concept of hybridisation, in the light of Kuhn's insights. There has been no ambiguity as to who discovered this concept, when it was first in print, and how important it was. The full-fledged form of the concept was published in 1931 independently by two American scientists John C. Slater (1900–1976) and Linus Pauling (1901–1994), although both of them had made their ideas public earlier: Slater at the American Physical Society meetings in 1930, and Pauling in the *Proceedings of the National Academy of Sciences* in 1928. Slater and Pauling both argued for the necessity of using an *s* orbital as well as three *p* orbitals in the carbon atom in order to explain carbon's four valences and the tetrahedral structure of methane. The metaphor 'hybridisation' for denoting this mix of *s* and *p* orbitals was first used by Robert S. Mulliken and J. H. Van Vleck before gaining currency with the scientific community around 1935.² The concept of hybridisation was indeed indispensable for extending the quantum-mechanical interpretation of the chemical bond as an electron pairing from diatomic molecules to polyatomic ones.

To be sure, the emergence of hybridisation attests to scientists' growing interest in exploring the borderland between physics and chemistry, a trend that led to the creation of physical chemistry in the late nineteenth century and of chemical physics and quantum chemistry in the 1920s and 30s. Slater and Pauling themselves experienced and on many occasions talked about the fruitfulness of interdisciplinary research; and historians have legitimately illuminated their works by examining them in this broad context.³ Yet the careful analysis of their research notes and published papers reveals that Slater and Pauling were working in quite disparate disciplinary traditions, with different approaches, for different audiences, and towards different goals. The aim of this paper is to explore their different routes to a common destination—hybridisation—and thereby to explicate tensions existing between physics and chemistry amidst the institutional and conceptual overlapping of the two disciplines.

2. The Slater Determinant and its Applications

For Slater, the concept of hybridisation was an outcome of his quest for a general quantum mechanical formalism to deal with atoms and molecules, and at the core of this research programme was his 'determinantal method' of setting up wave functions for the many-electron system. Therefore, my examination of

² See Mulliken (1931, p. 365); Van Vleck (1932); and Van Vleck (1933). Pauling and Slater did not use the term 'hybridisation' until 1935.

³ See Servos (1990); Nye (1992); Gavroglu and Simões (1994); and Hiebert (1996).

Slater's case will be focused on the years between 1929, when he developed the determinantal method, and 1931, when he finally published papers on hybridisation.

The gateway toward the many-body problem was the treatment of helium, a two-electron system, and it was opened by Werner Heisenberg in 1926. Basically, Heisenberg understood the interaction of two electrons in helium as a perturbation problem (Heisenberg, 1926). First, he assumed the unperturbed state where the two electrons were so far apart that their interaction could be ignored. He then set up the unperturbed wave functions of electrons as an approximation to the real solution. And finally, he solved the Schrödinger equation for the perturbed system with these approximate wave functions. In the course of this treatment, Heisenberg made two significant observations. One was that the energy split caused by the perturbation had to do with what he called the 'exchange integral'. This term arose from the indistinguishability of electrons, which led him to consider the exchange of electrons in setting up the approximate wave functions. The other was about the reinterpretation of the Pauli exclusion principle in terms of the symmetry property of wave functions. Heisenberg found that only those wave functions which were antisymmetric in the coordinates of the electrons would vanish if the electrons were assigned the same values of four quantum numbers. This was the forbidden state according to the exclusion principle, and thus Heisenberg replaced this principle with the statement that the wave function for the electrons should be an antisymmetric function for the coordinates at a given spin orientation.

With the treatment of electronic interactions and the reinterpretation of the exclusion principle, Heisenberg's helium paper laid the foundation for the further investigation of many-body problems. John C. Slater, a physics instructor at Harvard University, adopted this foundation, as many other theoretical physicists at that time did. But Slater was not content with Heisenberg's way of handling the spin dependence of the wave function, that is, his consideration of two separate antisymmetric wave functions with spin up and spin down. This way led several European physicists, such as Eugene Wigner, Friedrich Hund, Walter Heitler, and Hermann Weyl, to introduce group theory into many-body problems. Having no background in group theory and finding no good texts available, Slater was displeased with the situation that made everyone feel that 'to be in the mainstream of quantum mechanics, one had to learn about it' (Slater, 1975, p. 62).

In the winter of 1928, Slater sought to incorporate the spin and its quantum number into the wave function without using group theory, and the key idea was to regard the spin quantum number as a coordinate. As he summarised the determinantal method in his seminal paper published the next year: 'each electron has a wave function—a function of its coordinates (and, as we shall describe presently, of a coordinate representing its spin) depending on the [four quantum] numbers $n l m_l m_s$, which is a solution of Schrödinger's equation for a particle in a central field. We can denote the function of the i th electron by $u(n_i/x_i)$, where n_i stands for the four numbers $n_i l_i m_{li} m_{si}$, and x_i symbolizes the

four coordinates (three of position, one of spin) of the *i*th electron'. The next procedure was then to build an antisymmetric function conforming to the exclusion principle.

Now it is well known that the product of these functions, for all the electrons (1 ... *N*) of the atom, gives a function which approximately satisfies Schrödinger's equation. That is, $u(n_1/x_1)u(n_2/x_2) \dots u(n_N/x_N)$ is an approximate solution. But it is not antisymmetric in the electrons, so that it does not satisfy the exclusion principle. To build up an antisymmetric function we first note that we still have an approximate solution, connected with the same energy value, if we interchange any two *x*'s, obtaining for example $u(n_1/x_2)u(n_2/x_1) \dots u(n_N/x_N)$. We still have an approximation with the same energy if we make a linear combination of any such solutions. Then we can make the one possible combination which is antisymmetric, and it will both satisfy the exclusion principle, and will be an approximation solution of Schrödinger equation. This combination is conveniently written as a determinant:⁴

$$\begin{vmatrix} u(n_1/x_1) & u(n_1/x_2) & \dots & u(n_1/x_N) \\ \dots & \dots & \dots & \dots \\ u(n_N/x_1) & u(n_N/x_2) & \dots & u(n_N/x_N) \end{vmatrix} \quad (1)$$

The convenience was the hallmark of the determinantal method. Slater himself showed it in his treatment of complex atoms, not just verifying Hund's scheme for multiplet classification but giving detailed formulas for the separation between the energies of various multiplet states (Slater, 1929). Most physicists, especially those who saw group theory as an arcane, incomprehensible mathematical manipulation, welcomed the determinantal theory. 'No other work I have done', Slater later recalled, 'was so universally popular'.⁵

Slater moved on to the problems of complex molecules while spending several months of 1929–1930 in Leipzig as a Guggenheim Fellow. The distinctive property of molecules was the interatomic force, and Slater was convinced that the determinantal method would be useful in creating a generalised theory for this force, regardless of the kinds of molecules—whether they were diatomic molecules, polyatomic molecules, or metals. As for metals, two theories had already been developed: one by Heisenberg, in which a wave function consisted of the assignment of electrons to atoms; and the other by Felix Bloch, in which a wave function was set up with electrons moving across atoms.⁶ Although both theories could explain such metallic properties as ferromagnetism and conductivity, they had quite diverse accounts of the nature of the cohesive force holding a metal together and the situation of electrons in it. To examine the relationship

⁴ Slater (1929, pp. 1299–300). For the invention of the determinantal method, see Schweber (1990, pp. 373–378) and Slater (1975, pp. 58–65).

⁵ Slater (1975, pp. 62–63). See also Schweber (1990, p. 377).

⁶ Heisenberg (1928) and Bloch (1929). For the importance of these theories, see Hoddson, Baym and Eckert (1992).

between them, Slater took the example of the hydrogen molecule, the simplest case having an interatomic force, and illustrated how its wave functions were constructed in Heisenberg's and Bloch's schemes. This examination, published in the paper 'Cohesion in Monovalent Metals', became an insightful comparison between what would be known as the valence bond method and the molecular orbital method.⁷

At the outset, Slater mentioned two facts: 'first, that we must amplify Heisenberg's method by including polar states, to make it general enough to agree with Bloch's and to permit conductivity; second, that although Bloch has the proper set of functions, he has nowhere attempted to solve the perturbation problem, but has merely taken his unperturbed functions as being correct, which amounts to getting the energy to the accuracy of the conventional "first order perturbations"' (Slater, 1929, p. 512). The recognition of these facts pointed the way to comparing the two methods. In the first place, Slater distanced himself from the recent treatment of H₂ by Walter Heitler and Fritz London. Their study was indeed a straightforward outgrowth of Heisenberg's work on helium.⁸ They approximated the wave function with a linear combination of products of atomic orbitals, $a(1)b(2)$ and $b(1)a(2)$, where a and b denoted wave functions of two hydrogen atoms, and 1 and 2 represented each electron's coordinate; and then they considered the spin orientation of electrons, α (spin-up) and β (spin-down), to satisfy the Pauli exclusion principle. Although Slater agreed with Heitler and London that the concept of electron exchange, or resonance, would be essential in drawing the physical picture of the interatomic force,⁹ he did not adopt their way of handling the electron spin. Now, with his determinantal method, Slater was able to construct antisymmetric wave functions of both coordinates and spins. He considered four available functions ($a\alpha, a\beta, b\alpha, b\beta$), which were the products of atomic orbitals and spin wave functions; from them, two should be chosen to accommodate the two electrons of the hydrogen molecule. So, there were $4!(2!)(2!) = 6$ different wave functions possible: $(a\alpha)(b\alpha)$; $(a\alpha)(a\beta)$; $(b\alpha)(b\beta)$; $(a\alpha)(b\beta)$; $(a\beta)(b\alpha)$; $(a\beta)(b\beta)$. Slater then said:

The terms consist of one triplet and three singlets. Among the four terms $[(a\alpha)(a\beta), (b\alpha)(b\beta), (a\alpha)(b\beta), (a\beta)(b\alpha)]$ with M_S [the total spin angular momentum] = 0, the first two are polar (and not considered by Heitler and London, or Heisenberg), the last two are non-polar. Immediately one finds that the sum of these non-polar functions is the component of the triplet. We are then left with

⁷ Slater (1930a). For Slater's view on molecules and metals, see Schweber (1990, p. 379) and Assmus (1993, pp. 1–33).

⁸ Heitler and London (1927). For the origin and reception of Heitler and London's treatment, see Gavroglu and Simões (1994) and Gavroglu (1995).

⁹ Slater wrote a letter to Edwin C. Kemble, stating his confidence in Heisenberg's resonance. He said: 'You remember that I want to work out general methods of solving problems in solids. [...] The physical picture which I think is undoubtedly correct is that the interaction forces are much as in diatomic molecules, determined by resonance phenomena and I want to fit that in with the problem of many atoms' (Slater to Bridgman, 22 July 1929, quoted in Schweber (1990, p. 379)).

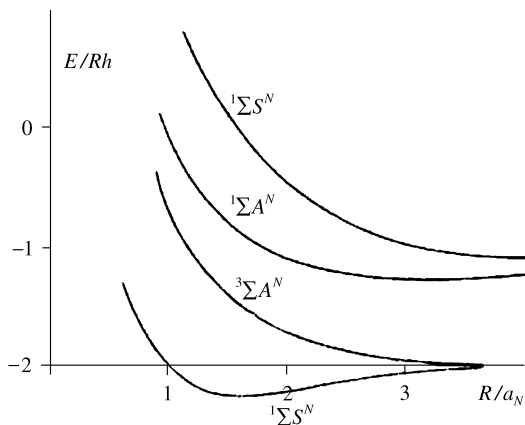


Fig. 1. Energy levels of H_2 drawn by Slater. The internuclear distance R and the energy E are in the Bohr atomic unit and in Rydberg energy unit, respectively.

three functions: the two polar ones, and the difference of the non-polar ones, from which to find our three singlets. The difference of the polar ones is antisymmetric in the nuclei, giving one state; their sum, and the difference of the non-polar functions, give two functions symmetrical in the nuclei, between which we finally solve the simple perturbation, resulting now in a quadratic secular equation, and obtain the two remaining singlet states (Slater, 1929, pp. 513–514).

This part of his paper may be difficult to follow without knowing the underlying manipulation of antisymmetric functions represented by determinants.¹⁰ But the outcome—one triplet and three singlets—could be given simply in a diagram plotting the energy levels as a function of the distance of separation (Fig. 1).

Slater found that the curve for the triplet term (the second lowest curve) was exactly the same as the repulsive state of Heitler and London, the wave function of which was $[a(1)b(2) - a(2)b(1)][\alpha(1)\beta(2) + \alpha(2)\beta(1)]$. The energy curve for the lowest singlet was represented by the wave function $[a(1)b(2) + a(2)b(1) + a(1)a(2) + b(1)b(2)][\alpha(1)\beta(2) - \alpha(2)\beta(1)]$. This was very similar to Heitler and London's attractive state, although it contained quite an appreciable contribution from the polar state. The other two singlet curves essentially represented the polar states.

Slater also showed that the same result could be obtained from Bloch's scheme. He was thus able to argue that Heisenberg's scheme, if polar functions were added to it, led essentially to the same kind of linear combination of wave functions as in Bloch's. The polar functions accounted for the ionic state in molecules and the state of free electrons in metals. Without elaboration, Slater

¹⁰ For the use of Slater determinants, see Park (1999, pp. 60–61).

concluded, each scheme had its own merits in different areas: Heisenberg's functions approximated the real wave functions better for *large* separation of atoms (the extended state), whereas Bloch's worked better for *small* separation (the compressed state) (Slater, 1929, pp. 515–516).

While making this comparison, Slater was in favour of Heisenberg's approach adapted by his determinantal method. His research notes of early 1930 reveal that he explored polyatomic molecules from this perspective. For example, he attempted to solve the challenging problem of methane, which had ten electrons, six from the carbon atom and four from four hydrogen atoms. Among these, two electrons were in the inner-shell (K-shell) of carbon, and the other eight were outside. The problem was then reduced to an eight-electron system, assuming no interaction between electrons of the inner- and outer-shells. To describe this system, Slater considered four $1s$ wave functions from four hydrogen atoms, and $2s$, $2p_+$, $2p_0$, and $2p_-$ from carbon—here, we can see the germ of the concept of hybridisation. Taking into account the spin states of each electron, there were then sixteen available functions, among which the eight electrons should be distributed. It was impossible to solve this problem like the hydrogen problem, since there were too many ways of making antisymmetric wave functions, i.e. $(16)!/(8!)(8!)$. At this point, Slater adopted an insight from Heitler and London's approach that the chemical bond was formed when atoms approached one another with their electrons having different spin orientations. He wrote: 'presumably the lowest state will come when all spins of C point one way, those of the H's opposite'.¹¹ This measure allowed him to consider only two cases: when the four electrons of carbon were all spin up and those of hydrogen spin down; and vice versa. Then antisymmetric wave functions could be represented by the determinantal forms. The computation of energy with these wave functions, however, was still formidable, and the explanation of methane's tetrahedral structure was not yet feasible.

To get an insight for further simplification of the methane problem, Slater turned to a simpler case that had two bonds, instead of four.¹² First, he tried a direct application of Heitler and London's approach. He assumed that there were four available wave functions, $u(a)$, $u(b)$, $u(1)$, and $u(2)$, and four electrons to fill. When bonds were made between $u(a)$ and $u(b)$, and between $u(1)$ and $u(2)$, it was possible to set up symmetric orbital wave functions for each bond. He then combined them to obtain the following expression:

$$[u(a/x_1)u(b/x_2) + u(b/x_1)u(a/x_2)][u(1/x_3)u(2/x_4) + u(2/x_3)u(1/x_4)], \quad (2)$$

where x_1, \dots, x_4 denoted coordinates of electrons. If this was denoted by $\Psi(1234)$, one could get such functions as $\Psi(1243)$, $\Psi(1423)$, etc., considering other kinds of bond formation and the possibility of electron exchange. Thus the appropriate form of wave function was the antisymmetric combination of all of

¹¹ Slater's research note (25 February 1930), *JSP*: 'Slater, Scientific Notes, Jan–Apr., 1930, Part I'.

¹² Slater's research note (26 February 1930), *JSP*: 'Slater, Scientific Notes, Jan–Apr., 1930, Part I'. Slater dealt with this case without specifying the molecule.

the twenty-four (4!) symmetric functions. Then Slater showed that one could start from the antisymmetric wave functions to build up the same combination. To this end, he considered four possible sets of antisymmetric wave functions: $\{u_x(a)u_\beta(b)u_x(1)u_\beta(2)\}$, $\{u_\beta(a)u_x(b)u_x(1)u_\beta(2)\}$, $\{u_x(a)u_\beta(b)u_\beta(1)u_x(2)\}$, and $\{u_\beta(a)u_x(b)u_\beta(1)u_x(2)\}$. Each set could be represented by the determinantal form, and, by manipulating each determinant, Slater obtained the same combination of wave functions as in 'the symmetric method'. Furthermore, a rough energy consideration led him to the same conclusion that Heitler and London had reached: the exchange integral was mostly responsible for the bond energy.¹³ Still, the rigorous calculation of the bond energy was out of reach, and the explanation of directional properties of molecules was not yet given. From this study of the simplified two-bond molecule, however, Slater gained confidence that his determinantal method was applicable to polyatomic molecules, as an extension of Heitler and London's approach.

A few months after his return to Harvard, Slater gave a talk in an informal session at the meeting of the American Physical Society on 24–26 April 1930. It is difficult to know what he really talked about, and how far his moving back and forth between various ideas and methods led him to the concept of hybridisation.¹⁴ According to the draft of his paper written in October 1930, the general idea of the directional property of valence had already been presented at the April meeting.¹⁵ To be sure, before that meeting, Slater had found that electrons in p orbitals, unlike those in s orbitals, might be responsible for the spatial arrangement of valence. On 19 April, he added to his previous research note a drawing of p orbitals in order to illustrate the directional property of the two-bond molecule, such as H_2O . But it is still uncertain whether he set up wave functions for it and obtained the energy expression; and whether he dealt with such molecules as methane in which s as well as p orbitals should be mobilised to make four bonds.

The several months' gap between April (when he presented his idea informally) and October (when he wrote a draft of the paper) can be partly attributed to a change in Slater's institutional affiliation. In May, he received an offer of the chairmanship of the physics department at MIT from Karl T. Compton, the university's newly-elected President. Compton had been deeply interested in Slater for many years. While in the Princeton physics department, Compton had tried to lure Slater to Princeton twice, in 1927 and 1929, but with no success; each time, Harvard had countered Princeton's offer and promised to accept Slater's proposal for revamping the entire graduate curriculum and revising the research programme of the Jefferson Physical Laboratory. Slater envisioned new physics education and research being firmly based on 'fundamentals', such

¹³ *Ibid.*

¹⁴ Because his talk was in an informal session, its abstract did not appear in the *Bulletin of the American Physical Society*.

¹⁵ Slater's draft of the paper entitled 'The Directional Properties of Valence from p Electrons' (10 October–15 November 1930), *JSP*: 'Slater, Scientific Notes, Jan–Apr., 1930, Part II'.

as the quantum theory which could be applied to problems of atoms, molecules, metals, and crystals. To implement this goal, he demanded not only close cooperation between theorists and experimentalists but also effective coordination of efforts between the physics and other departments. In 1930, given the slow progress in reform at Harvard, Slater saw a greater opportunity at MIT to accomplish his vision; so he accepted Compton's offer with little hesitation.¹⁶ Most importantly, as he moved to MIT, he had a tool—the determinantal method—with which to attack diverse physical problems. 'It probably was a fortunate thing', he wrote later,

that this move to a position which could have absorbed all my efforts in administrative work came at a time when I had just developed the new determinantal method. For that method opened possibilities in practically every branch of atomic, molecular, and solid-state theory. These had all been held waiting for a manageable treatment of the many-body theory, and this was just what the method gave. I had so many ideas regarding applications of the method, some of which I worked out in Leipzig, that many of these were still in the process of being worked out when I went to MIT. [...] I had more students and postdoctoral workers at MIT than I had had at Harvard (I had not directed any doctoral students there), continued to teach courses, started to write books, and in general was able to make a greater scientific contribution there than I could have if I had stayed where I was (Slater, 1975, pp. 64–65).

3. The Directional Properties of Valence

The determinantal method was the centre piece of Slater's research programme in general, and of his investigation of molecules in particular. When he wrote a draft of 'The Directional Properties of Valence from p Electrons' in October 1930, Slater depicted this work as a sequel to his paper on metals in terms of using the determinantal method. He started the draft by mentioning the distinctive feature of valence in polyatomic molecules, where the relative positions of atoms, as well as their distances of separation, were highly significant. The previous theory of valence, especially that of Heitler and London, did not consider the directional properties of the chemical bond; for it was based on the study of diatomic molecules, where the energy curve was given only as a function of the distance of separation. 'It appears, however', Slater said, 'that wave mechanics has now reached a point where it can derive certain conclusions about these problems, and can in fact attack the general problem of valence. This results largely through the simplification in the treatment of the spin introduced by the writer in the problem of atomic structure, and already used in the problem of cohesion of monovalent metals'.¹⁷

¹⁶ For Slater's efforts to revise the physics education and research at Harvard, see Schweber (1990, pp. 360–366).

¹⁷ Slater's draft of the paper entitled 'The Directional Properties of Valence from p Electrons' (10 October–15 November 1930), *JSP*: 'Slater, Scientific Notes, Jan–Apr., 1930, Part II'.

In addition to these introductory remarks on the polyatomic molecular problem, the October draft had two more parts. In one part, Slater discussed the empirical evidence regarding the localisation of chemical bonds between pairs of atoms and the spatial orientation of the bonds; he drew on well-known structural information about such molecules as water (triangular), ammonia (pyramidal), and methane (tetrahedral). He also mentioned the Lewis theory of the shared-electron pair bond as an inductive theory built from the empirical data. In another part of the draft, he illustrated, with the diatomic case of H_2 , how to set up antisymmetric wave functions and calculate energy levels from them. Slater did not go into the details of the polyatomic cases, but he was certainly aware that in order to deal with four-bond molecules, a linear combination of s and p orbitals had to be made. This was essentially the expression of the hybridisation concept.¹⁸

On 30 December 1930, Slater presented the paper 'Directed Valence in Polyatomic Molecules' at the American Physical Society meeting held in Cleveland. The abstract clearly indicates that he ascribed the spatial orientation of p orbitals or their mix with s orbitals to the directional property of valence.

By means of wave mechanics one can draw conclusions regarding valence in polyatomic molecules, finding in particular that the different shared electron bonds from a single atom tend to be at definite angles to each other. The two bonds in atoms like oxygen, and the three in nitrogen, tend to be mutually perpendicular, while in carbon a tetrahedral structure is indicated. These conclusions in the first two cases rest on the nature of the wave function for a p electron: the three types of p electron may be considered to have densities largely along three mutually perpendicular directions. With carbon, one must combine these three with an s electron to produce tetrahedral valences. The conclusions can be supported by a wide range of experimental facts, from the structure of simple inorganic molecules, metals, and organic compounds (Slater, 1930b).

Returning from the meeting, Slater immediately published the paper.¹⁹ Here, we can see his detailed account—though still qualitative rather than quantitative—of directed valence. As in his October draft, Slater began the published paper by describing the importance of the determinantal method in dealing with the problems of complex atoms, metals, and polyatomic molecules. By now, his confidence was shored up by the arrival of Max Born's paper that applied the determinantal method to diatomic molecules in general without using group theory (Born, 1930). Slater then summarised his notion of the chemical bond—a pairing of two electrons of opposite spin directions: 'Two atoms containing all their electrons in closed shells repel each other. But if each atom has one wave function containing only one electron, rather than two of opposite spins, attraction is possible. This actually occurs if the spins of the electrons in question

¹⁸ *Ibid.*

¹⁹ Slater (1931a). It was received on 22 January 1931.

in the two atoms are oppositely directed'. He also described the attraction figuratively, something like the overlap of orbitals (Slater, 1931a, p. 481). For example, as a 'tentative' explanation, he visualised the bond-forming process in CH_4 : 'the three hydrogens attached to p valences would form a pyramid, as in NH_3 , and the remaining hydrogen bound to an s , and free to wander, would set itself opposite the apex of the pyramid to avoid the others, forming a rough tetrahedron. This would not be a symmetrical tetrahedron, however; and by a slight change in the conditions we can arrive at a really symmetrical one, which would undoubtedly have a lower energy, and which we consider to be the real form for a tetravalent compound' (Slater, 1931a, pp. 485–486). To arrive at this symmetrical arrangement, Slater proposed to set up a new kind of orthogonal function by four linear combinations of three p orbitals and one s orbital; yet he gave no example of these combinations and provided no discussion of how they led to a lower energy.

The theoretical justification of directed valence came in the paper 'Molecular Energy Levels and Valence Bond', which Slater wrote while spending the summer of 1931 at the University of California, Berkeley (Slater, 1931b). If his previous paper had used particular examples to illustrate universal properties of polyatomic molecules, this one proceeded in the opposite direction, from general principles to particular cases. Slater first reviewed the perturbation theory to elucidate the steps necessary for making approximations to the real solutions of the problem; the steps included setting up the unperturbed wave functions, determining the 'matrix components' of energy, and solving the 'secular equation'. Next he examined each step in detail: he showed how to obtain the unperturbed functions from atomic orbitals with his determinantal method; he discussed what kind of integrals should be computed as the matrix components and what terms could be neglected; and he suggested the way to simplify the secular equation, considering the spin state of the system in question. Finally, he dealt with real problems categorically, such as 'two atoms, each with one s electron', 'two atoms, one s and one p ', and so on. Methane belonged to the case 'five atoms, one with four s and p electrons, the others with an s electron each'.

The overall purpose of the paper was to lay out the procedure for solving the Schrödinger equation for molecules in general, rather than to carry out computations for actual examples (see also Slater (1975, p. 105)). Perhaps Slater thought he could leave those computations as good thesis topics for his graduate students. Most importantly, Slater sought to set up a theoretically correct approximation as far as he was able to do so, rather than making dubious approximations for computational practicality from the beginning. Therefore, when he discussed the matrix components of energy, he said: 'It is much safer to formulate the problem in a general way, including all electrons of the problem, as we have sketched here, and then eventually to show that some terms are independent of interatomic distance and lead to atomic energies, than just to start out as if the atoms consisted only of valence electrons surrounding a nucleus of some effective nuclear charge, even though the latter method gives

qualitatively the correct interpretation of multiplet levels, and so on' (Slater, 1931b, p. 1117). Slater was a critical examiner of every step of approximation (the neglect of terms, the simplification of the problem, the use of empirical data, and so on), rather than someone who would make actual computations.

It is doubtful, however, whether many chemists benefited from Slater's theoretical layout. It provided a set of problems but had no computed solutions, except for those already solved. For instance, Slater discussed the methane molecule still without attempting to derive four linear combinations of the p and s orbitals that could lead to the lowest molecular energy level. In short, although he dealt with valence and the electronic structure of molecules—fundamental questions in chemistry—his paper was not suitable for chemists to read. Chemists might have found his pictorial illustration of directed valence in his earlier paper more congenial, but there, the importance of the determinantal method was asserted rather than shown. The reading of both papers was required to understand Slater's aim and method. Otherwise, his research programme of applying the determinantal method to atomic, molecular, and metallic problems was not so recognisable. But chemists did not have to understand Slater's lengthy theoretical considerations to use the concept of hybridisation; Linus Pauling also presented this concept almost at the same time with a shortened mathematical justification but a convincing quantitative argument.

4. Pauling and the Nature of the Chemical Bond

Linus Pauling became interested in exploring the borderland between physics and chemistry during his graduate years at the California Institute of Technology.²⁰ But his view of a physical theory was not the same as that of a theoretical physicist. He was not particularly inclined to develop a physical theory *per se* or to scrutinise the soundness of its underlying assumptions. Instead, he sought to find the usefulness of a theory in explicating and correlating chemical phenomena, or tried to make it useful for chemistry by adding his own interpretations. In other words, his aim was not to reduce chemistry to physics, but to appropriate ideas from physics for the benefit of chemistry.

This attitude was already apparent in his paper 'The Dynamic Model of the Chemical Bond and its Application to the Structure of Benzene', written in 1925 (Pauling, 1926). Here, Pauling embraced the Bohr theory—ironically at the dawn of quantum mechanics—and attempted to use it for understanding the chemical bond. 'The continued success of the Bohr atom', he wrote,

has led all physicists except the most cautious to attribute a certain reality to the physical concept underlying the theory; namely, that the atom is composed of electrons rotating in stable orbits about the positive nucleus. The determination of

²⁰ There are already several biographies of Pauling. See, for example, Paradowski (1972) and Hager (1995).

these stable orbits can be made, in those cases that are simple enough to permit mathematical treatment, by the application of the principles of the quantum theory, thus verifying the correctness of the dynamic atom, since the quantum theory has been widely used in the explanation of the most varied phenomenon. Hence, *in attempting to explain the chemical properties of substances on the basis of the structure of the atom it would seem desirable to assume the Bohr theory to be true, and to make only those changes and additions which are necessary and logical extension of the theory* (Pauling, 1926, p. 1132; emphasis mine).

As Pauling later admitted, the dynamic model of chemical bonds based on Bohr's quantum theory was hypothetical and speculative (Pauling, 1970, p. 998). But it reflected what he looked for in the quantum theory: a better tool for explaining the bond types, the directed valence, the bond energy, and molecular and crystal structures. It is thus not surprising that after graduation, Pauling proposed to study 'the application of quantum mechanics to the problem of the structure of molecules and the nature of the chemical bond' during his postdoctoral trip to Europe as a Guggenheim Fellow.

Pauling returned to Caltech to be an assistant professor of theoretical chemistry in 1927, filled with confidence in the new mechanical framework. His confidence initially rested on Heitler and London's treatment of the hydrogen molecule, but it grew with their subsequent papers on its expansion to other molecules. His research notes of 1928 show that he studied the group theory from Heitler's papers. He also followed very closely London's discussion of valence, which included the resonance effect as the energy source of the non-polar bond of molecules in general, and the exclusion principle as the universal condition for electron pairing.²¹ Pauling was particularly intrigued by the way London explained the various valence numbers that an atom could have in forming molecules with other atoms. For example, atoms having five electrons in the outer-shell (such as N, P, As, Sb, and Bi) could have one, three, or five valences. London interpreted this variation in terms of the number of unpaired electrons in p ($l = 1$) orbitals alone, or together with s ($l = 0$) and d ($l = 2$) orbitals, the case accompanying changes in quantisation (London, 1928a, p. 470). By the same token, atoms having four electrons in the outer-shell (such as C, Si, Ge, and Sn) could have two or four valences, should s as well as p orbitals be made available for bonding (London, 1928a, p. 471).

London's theory of valence was not confined to ordinary molecules; he also dealt with ionic compounds like the ammonium ion (NH_4^+) and discussed the boundary between polar and homopolar bonding. Fascinated by its general applicability, Pauling drew possible electron configurations of simple atoms and ions according to London's theory, and then considered the molecular formation among them. Pauling found that London's theory was the 'simple' application of quantum mechanics, without elaborate mathematical considerations, yet

²¹ Pauling's research note, 'Group Theory and Chemical Combination', and 'London's paper. General ideas on bonds', in *LPP*: 240 (LP Notes & Calculations Vol. II, 1923–1929). The papers Pauling read were Heitler (1927, 1928) and London (1928a, b).

leading directly to an explanation of electron pairs and of the group of eight electrons (octet) for some elements. It was in simple cases 'fully equivalent to G. N. Lewis's ideas of the non-polar bond'. However, the 'quantum mechanics explanation of valence is more powerful than the old picture', he noted.

Many structures are at once eliminated by the Pauli exclusion principle: for example, no shared pair number greater than 4 for first row elements, or greater than 1 for H. Furthermore definite predictions can be made as to whether a compound is polar or non-polar or a transition compound. Many refinements and extensions of London's simple theory are also possible, involving the quantitative consideration of spectral and thermochemical data. These lead to a number of important conclusions regarding the hydrogen bond, the nature and occurrence of the double bond and triple bond, the stability of various valences, the structure of graphite and of the benzene ring, and so on.²²

In terms of the chemical applications of quantum mechanics, Pauling's aim was much broader than London's. In addition to the valence number and the distinction between polar and non-polar bonds, he sought to give a theoretical explanation of intermolecular interaction like the hydrogen bond, the origins of the double and triple bonds, and the stability and spatial orientation of valence. In short, he pursued a better understanding of the nature of the chemical bond. Indeed, Pauling's goal did not change after the time he toyed with the Bohr theory. Nor did his tactics. Even though exact solutions of the Schrödinger equation were available only for such simple systems as He, H_2^+ , and H_2 , Pauling did not hesitate to make quantum-mechanical interpretations of chemical ideas in a qualitative way. If necessary, he bolstered his interpretations with the quantitative consideration of empirical data rich in physics and chemistry, like those of atomic and molecular spectroscopy, X-ray crystallography, and thermochemistry. Pauling's goal and tactics were reflected in his discovery of the hybridisation concept.

5. The Maximum Bond Strength

The key idea of hybridisation—that the rupture of energy quantisation between *s* and *p* or *p* and *d* orbitals could occur in atoms having four or more valences—was not particularly Pauling's discovery, as London had already considered this possibility. Yet Pauling's nose smelled the chemical significance of this rupture. He posed two questions about it: what kind of atoms or ions were favourable for the changed quantisation?; and how was it related to the directional property of valence? His familiarity with thermochemical and spectral data helped him to answer the first question. In the case of carbon having four bonds, the bond energy was about 175 kcal from the heat of sublimation

²² Pauling's research note, 'London's paper. General ideas on bonds', in *LPP*: 240 (LP Notes & Calculations Vol. II, 1923–1929), pp. 22–23.

data, where the energy difference between s and p orbitals was 5.4 eV or 127 kcal from spectroscopic data.²³ Hence the energy stabilisation resulting from the formation of four bonds seemed to be large enough to change the quantisation. In the case of oxygen, however, the $s - p$ energy separation was about 14.4 eV or 340 kcal, which was larger than the energy $O + O \rightarrow O_2$. Thus the quantisation was not likely to be changed. Among the elements of the first row of the periodic table, the changed quantisation could occur for boron, carbon, and nitrogen, but not for oxygen and fluorine or their ions (Pauling, 1928, p. 361).

Once the energy quantisation was broken, s and p orbitals were no longer suitable for representing the energy state of the electrons. Therefore, it was necessary to form a new kind of atomic orbital, which would lead to the most stable bond formation and thus could account for the three-dimensional structure of molecules. In early 1928, Pauling strove to elucidate this relation between the changed quantisation of atoms and the spatial arrangement of valence.²⁴ As his first step for dealing with carbon's valence, he represented an s orbital and three p orbitals in polar coordinates, omitting the common factor $1/(4\sqrt{6\pi})(z/a_0)^{3/2}e^{-r/2a_0}$:

$$\begin{aligned}
 l = 0, \quad m = 0 \text{ (s orbital): } \quad \psi_1 &= a \\
 l = 1, \quad m = 0 \text{ (p}_0 \text{ orbital): } \quad \psi_2 &= \sqrt{3} \cos \theta \\
 m = 1 \text{ (p}_1 \text{ orbital): } \quad \psi_3 &= \sqrt{3} \sin \theta \cos \varphi \\
 m = -1 \text{ (p}_{-1} \text{ orbital): } \quad \psi_4 &= \sqrt{3} \sin \theta \sin \varphi,
 \end{aligned} \tag{3}$$

where $a = (1 - 2/r)\sqrt{3}$. As Slater described it in 1931, the ordinary procedure for solving the Schrödinger equation with the perturbation method required such steps as setting up antisymmetric wave functions from the above orbitals, obtaining the matrix components of the energy, and solving the secular equation. But that was not Pauling's concern. Instead, he just tried to prove that the energy of the system would be lowered by the linear combinations of s and p orbitals at certain values of θ and φ : for example, $\theta = \pi/2$ and $\varphi = (0, 2\pi/3, 4\pi/3)$ for the triangular quantisation (in ethylene); and $\cos \theta = \pm 1/\sqrt{3}$ and $\tan \varphi = \pm 1$ for the tetrahedral quantisation (in methane). He then treated the resultant expressions of p orbitals (0, 1, $\sqrt{3}$, etc.) at fixed angles and the s orbital expression (a) as if they were legitimate wave functions, using them in the calculation of the energy of systems. This energy calculation showed that tetrahedral and triangular systems were more stable when represented by the mix of s and p than when represented by p orbitals alone. 'Hybridisation', as this mix was later named, seemed to be vindicated as an essential concept for explaining the spatial orientation of valence.

²³ *Ibid.*, pp. 18–20.

²⁴ Pauling's research note, '1928, Early efforts at hybridization of bond orbitals', LPP: 274.5.

When Pauling sent a short note to the *Proceedings of the National Academy of Sciences* in March 1928, he was so confident about his treatment that he announced that the ‘detailed account of the material mentioned in this note will be submitted for publication to the *Journal of American Chemical Society*’ (Pauling, 1928, p. 362). It was not until April 1931, however, that he was able to publish the promised paper under the title of ‘The Nature of the Chemical Bond’ (Pauling, 1931a). Why did Pauling not publish his mix of *s* and *p* orbitals and the energy calculation in 1928, and what made him overcome a stumbling block in 1931? Pauling later mentioned the gap between 1928 and 1931 in an interview with John L. Heilbron:

Well, there was this gap because I was having so much trouble getting a result that was in simple enough form to be valuable to chemists and to have more significance than numbers that you would get out of a computer nowadays [the 1960s]. [...] It doesn’t mention hybridization [in the paper of 1928], but it is this paper in which this statement [of changed quantization] was made for the first time. I can do this hybridization and get some complicated expressions, you see, but having done that I didn’t feel satisfied, so it wasn’t until about December 1930 that I made the step of assigning the same radial function to the *s* orbital and the *p* orbital essentially.²⁵

In December 1930, Pauling wrote a draft of a paper titled ‘Eigenfunctions for Chemical Bonds’. He later claimed that he completed most of the calculations for it in one evening.²⁶ This draft already looked like a finished research product showing how hybrid orbitals accounted for molecular structures. As Pauling explained in the above interview, the key step was the assumption regarding the radial part of wave functions. It was in fact the starting point. He said: ‘I shall assume $R(r)$ [the radial part] to be the same for all eigenfunctions discussed’. He then represented eigenfunctions only in terms of their angular parts.

	maximum value
$s = 1$	1
$p \begin{cases} z = \sqrt{3} \cos \theta \\ x = \sqrt{3} \sin \theta \cos \varphi \\ y = \sqrt{3} \sin \theta \sin \varphi \end{cases}$	$\begin{matrix} \sqrt{3} = 1.73 \\ \sqrt{3} \\ \sqrt{3} \end{matrix}$
$d \begin{cases} d_z = \sqrt{5/4}(3 \cos^2 \theta - 1) \\ d_{1x} = \sqrt{15} \sin \theta \cos \theta \cos \varphi \\ d_{1y} = \sqrt{15} \sin \theta \cos \theta \sin \varphi \\ d_{2x} = \sqrt{15/4} \sin^2 \theta \cos 2\varphi \\ d_{2y} = \sqrt{15/4} \sin^2 \theta \sin 2\varphi \end{cases}$	$\begin{matrix} \sqrt{5} = 2.24 \\ \sqrt{15/4} = 1.94 \\ \sqrt{15/4} \\ \sqrt{15/4} \\ \sqrt{15/4} \end{matrix}$

(4)

²⁵ Interview with Linus Pauling by John L. Heilbron, Archive for the History of Quantum Physics, American Philosophical Society Library, Philadelphia.

²⁶ Pauling’s draft, ‘Eigenfunctions for Chemical Bonds’, *LPP*: 245. In 1975, Pauling added a note on the first page of this draft, saying that ‘this work was done in Dec. 1930, much of it in one evening’.

The comparison of this representation and the previous one of 1928 reveals the mathematical implications of the assumption: it regarded $(r - 2)\sqrt{3}$ (a part of the radial wave function of s) as the same as r (that of p), or to put $\psi_1 = a = (1 - 2/r)\sqrt{3}$ into 1. It allowed Pauling to compare s and p orbitals in an extremely simple way: while the spherically symmetric s had the ‘maximum value’ 1 in all directions, the three p orbitals had the ‘maximum value’ $\sqrt{3}$ along the z , x , and y axis, respectively.

Pauling then proposed the important idea that these maximum values would represent the ‘maximum possible strength’, should bonds be made between atoms; in other words, the bond-forming power or bond strength was gauged by means of the orbital’s maximum value. For instance, p electrons would form stronger bonds than s electrons; and when the bonds were formed by p electrons, they would be oriented at right angles to one another. Pauling elucidated hybridisation and its relation with molecular structures in the same way. He made linear combinations of (or hybridised) s and p orbitals for linear, triangular, tetrahedral structures, and so on; then he obtained the maximum value of the hybrid orbitals; and finally he compared it with the maximum value of s or p before hybridisation. To derive hybrid orbitals was not particularly difficult: with the conditions of normalisation and orthogonality, Pauling calculated a new set of hybrid orbitals for a given structure. For example, the tetrahedral structure had four hybrid orbitals, equivalent in their maximum values:

$$\begin{aligned}\psi_1 &= \frac{1}{2}s + \frac{\sqrt{3}}{2}z \\ \psi_2 &= \frac{1}{2} - \frac{1}{2\sqrt{3}}z + \frac{\sqrt{2}}{\sqrt{3}}x \\ \psi_3 &= \frac{1}{2}s - \frac{1}{2\sqrt{3}}z - \frac{1}{\sqrt{6}}x + \frac{1}{\sqrt{2}}y \\ \psi_4 &= \frac{1}{2}s - \frac{1}{2\sqrt{3}}z - \frac{1}{\sqrt{6}}x - \frac{1}{\sqrt{2}}y\end{aligned}\quad (5)$$

According to Pauling, the hybrid orbital for a linear molecule (sp hybridisation) had the maximum value, 1.93; for a triangular one (sp^2 hybridisation), 1.991; for a tetrahedral one (sp^3 hybridisation), 2. All of them were higher than the maximum value of s or p . He then moved on to explain other cases having hybridisation of d orbitals with s and p orbitals.

In the draft of his paper, Pauling made freewheeling use of the assumption that the radial part of wave functions could be neglected, and employed the idea of correlating the maximum value of orbitals and bond strength without justification. Hence it is not easy to trace how he got these ideas. Furthermore, his research output between 1928 and 1931 was primarily on the X-ray determination of crystals, not on quantum mechanics. Thus, when spending the

spring and summer of 1930 in Europe, he met X-ray crystallographers like Lawrence Bragg of Manchester and John D. Bernal of Cambridge, rather than quantum theorists. What brought him back to the theoretical studies of chemical bonds, and what allowed him to solve the hybridisation problem in one evening?

As Thomas Hager suggests, one possible source of stimulation was Slater (Hager, 1995, pp. 155–157). Pauling attended the April meeting of the American Physical Society in 1930 where Slater gave his informal talk about the directional properties of valence.²⁷ In addition, Pauling might have seen the abstract of Slater's talk for the December meeting, which was published in the *Bulletin of the American Physical Society* (Slater, 1930b). But contrary to Hager's argument, it was not the assumption of assigning the same radial function to s and p orbitals that Pauling might have taken from Slater. Slater never developed that assumption, or took the mathematical step based on it. In essence, the idea was Pauling's. In 1928, when juggling with ideas and mathematical steps to simplify the hybridisation problem, Pauling had considered putting $\psi_1 = a = 1$; but he had not pursued it further. Later in 1931, he justified the use of this assumption in terms of his study of many-electron atoms and ions (Pauling, 1931a, p. 1376, note 22). Therefore, the new idea in December 1930 was the correlation of the maximum value of orbitals and bond strength.

Pauling's paper 'The Nature of the Chemical Bond' of April 1931 was essentially based on his draft of December 1930, but it was organised in an entirely different way. Pauling first postulated six 'rules' regarding the properties of the electron-pair bond, before dealing with specific cases. Among them, the fifth rule contained his idea about the maximum value of orbitals and bond strength, together with the assumption about the radial part of wave functions: 'Of two eigenfunctions with the same dependence on r , the one with the larger value in the bond direction will give rise to the stronger bond, and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction' (Pauling, 1931a, pp. 1368–1369). All of the six rules were not mathematically derived from quantum mechanics; rather, they came from interpretations Pauling made by the 'qualitative consideration of the factors influencing bond energies'. And Pauling's interpretations were predicated on Born's 1930 treatment of the interaction of two atoms, which employed Slater's determinantal method for making antisymmetric wave functions.²⁸

Pauling was well informed about the difficulty involved in the rigorous treatment of many-electron systems. He was equally well aware that his main

²⁷ Slater acknowledged his indebtedness to discussions with Pauling and Eyring among the people who attended the April meeting. See Slater's October draft.

²⁸ In his justification of three rules, Pauling mentioned Born's treatment and Slater's method: 'The construction of this eigenfunction [of electrons in bond formation] and the evaluation of the integral would be very laborious; it will be noted, however, that this problem is formally similar to Born's treatment of the interaction of two atoms in S states, based on Slater's treatment of atomic eigenfunctions' (Pauling, 1931a, p. 1369).

audience—chemists—would not appreciate the formidable array of symbols and equations necessary for the formal justification of the electron-pair bond. He thus provided in his paper only a ‘sketch’, in a smaller font than usual, of how he conceived the rules about eigenfunctions (Pauling, 1931a, pp. 1369–1370). It was what he called an ‘inclusive proof’, extracting meaningful results from Born’s study of diatomic molecules to discuss the chemical bond in general. In the first place, Pauling considered the energy expression that Born had obtained:

$$E = W_A + W_B + J_E + J_X - {}_Y J_Y - {}_Z J_Z, \quad (6)$$

where E was the energy of the diatomic molecular system, W_A and W_B were the energies of the separate atoms, and A , B , and J_E represented the Coulomb interaction of A and B , neglecting resonance. The resonance term J_X corresponded to an exchange of the two electrons from A and B participating in bond formation; J_Y corresponded to an exchange of the bond electron from B with a paired electron with similarly directed spin on A , or vice versa; and J_Z corresponded to an exchange of a paired electron on A with one on B . The resonance integrals, J_X , J_Y , and J_Z , were found to have negative signs in most cases. Pauling paid particular attention to the way these integrals might be determined visually. He said that the ‘resonance integrals depend qualitatively on what may be called the *overlapping* of the single-electron eigenfunctions involved; if ψ_A and ψ_B are two single-electron eigenfunctions, the product $\psi_A(1)\psi_B(2)\psi_A^*(2)\psi_B^*(1)$ occurs in the resonance integral corresponding to the permutation involving electrons 1 and 2, and the value of the integral increases as the magnitude of this product in the region between the two nuclei increases’. In this way, Pauling devised a means of thinking about the values of integrals without calculating them. This helped him to consider how the resonance integrals contributed to the energy of the system, which would be more stable should the energy E have a greater negative value. Therefore, he argued:

The positive sign preceding J_X requires that the two bond eigenfunctions ψ_A and ψ_B show the maximum overlapping in the region between the two nuclei, while the negative sign preceding J_Y requires the minimum overlapping between ψ_A and the eigenfunction B other than ψ_B , and between ψ_B and the eigenfunctions of A other than ψ_A . Hence the correct zeroth-order eigenfunctions for the atom A are such that one, the AB bond eigenfunction ψ_A , extends largely in the direction of atom B , while the other A eigenfunctions avoid overlapping with ψ_B . As a consequence the integral J_X is of large magnitude, while the integral J_Y , because of the small overlapping of the eigenfunctions involved, are small (Pauling, 1931a, p. 1370).

In short, Pauling found in Born’s paper theoretical grounds for what was soon called the ‘criterion of maximum overlapping’. And it seemed to Pauling that this criterion justified his use of the maximum value of orbitals in measuring their bond-forming power, allowing him to obtain hybrid orbitals in a simple way. Such hybrid orbitals could be considered angular parts of zeroth-order eigenfunctions, ready to be put into perturbation energy calculations. But

Pauling neither formulated the secular equation for the perturbation calculations of polyatomic molecules, nor attempted to compute integrals that might appear as matrix components. In terms of his use of quantum mechanics, he did not go beyond the point where he obtained hybrid orbitals and their maximum values. Back in 1928, by contrast, he had tried to show the energy stabilisation effect of hybridisation by the perturbation calculations, although his calculations had been very much simplified, doubtful, and unsatisfactory even to himself. In 1931, the perturbation calculations still being difficult, Pauling relied on visual interpretations of resonance integrals in Born's energy expression to explain bond strength, hybridisation, and the directional properties of valence. Even though he did not solve the Schrödinger equation, Pauling's theory of valence looked very much like a deductive system: quantum mechanics begot a set of interpretative rules, and the rules justified his treatment of molecules. This was a coherent picture that encompassed diverse chemical phenomena, ranging from the relative strengths of bonds formed by different atoms to the spatial arrangements of bonds, and from the magnetic properties of molecules to the rotational constraints about bond axes. Pauling was confident that chemists would like this picture.

Here, Slater's intellectual influence upon Pauling could be seen indirectly through Pauling's use of the treatment of diatomic molecules by Born: at least, Pauling acknowledged it that way. There is no doubt, however, that the news about the publication of Slater's paper on the directional property of valence made Pauling speed up the publication of his own paper. Pauling did not want to be beaten in the race for the discovery of hybridisation. He asked the editor of the *Journal of the American Chemical Society* for the prompt publication of his paper.²⁹ In addition, he also sent a letter to the editor of the *Physical Review*, calling the paper to the attention of physicists (Pauling, 1931b). This notification was not so much intended to capture a physical audience as to secure his credit in the quantum-mechanical study of valence over Slater. Pauling mentioned his preliminary announcement of hybridisation made three years earlier and boasted of his 'very simple but powerful approximate *quantitative* treatment of bond strengths'. He also described the wide range of his study, including the magnetic moments of polyatomic molecules and complex ions and the determination of molecular and crystal structures. Moreover, Pauling summarised the work by Slater to differentiate it from the original part of his own research. 'Three of these results have been independently obtained by Slater and announced in a preliminary communication', Pauling said (1931b, p. 1186).

He [Slater] points out the possibility of the formation of four equivalent tetrahedral bonds by a carbon atom (as I did in 1928), without giving the tetrahedral eigenfunctions and without recognizing that tetrahedral eigenfunctions are also important when fewer than four bonds are formed; and mentions that this leads to

²⁹ Pauling to A. B. Lamb (11 February 1931), quoted in Gavroglu and Simões (1994, p. 81). See also Hager (1995, p. 159).

restricted rotation about a double bond. Having apparently assumed the importance of one single electron eigenfunction to bond formation, he also show that p eigenfunctions should lead to 90° bond angles.

6. Conclusion

What Slater and Pauling discovered was not a new material or a phenomenon, but a new mode of explaining a known property of molecules, their structure. While Pauling was concerned about sharing credit for the hybridisation concept, Slater generously accepted the ‘independence’ of their discoveries (Slater, 1931b, p. 1109). No controversy arose over this matter; and both names were inscribed into the ‘Heitler–London–Slater–Pauling’ (HLSP) theory for their contributions in expanding Heitler and London’s interpretation of valence to polyatomic molecules.³⁰ Even the Berkeley physicist R. T. Birge, who suspected that Pauling was ‘duplicating some of Slater’s work’, praised Pauling’s paper as an ‘article of the very highest importance’.³¹ For Pauling, it was only the beginning of a series of seven papers on ‘The Nature of the Chemical Bond’, which earned him national prominence. By the end of 1931, he became a full professor at Caltech, the first winner of the prestigious Langmuir Prize of the American Chemical Society, and an authority on the chemical applications of quantum mechanics.³²

While Slater found Pauling’s hybridisation acceptable as the same qualitative verification of the directional property of valence as his was, he did not agree with the way Pauling made quantitative arguments. To Slater and other physicists like Mulliken, the quantity that Pauling called the bond strength was problematic. For Pauling’s bond strength was far from representing overlap integrals, which were responsible for bond energy. This quantity, if only the angular part of wave functions was considered, was by no means proportional to the overlap integral, and its implicit assumption that the overlap integrals would be the same for an s orbital and a p orbital was not well grounded in quantum mechanics. According to Pauling’s recollection, Slater and Mulliken ‘started out right away saying that this wasn’t much good and they continue to say it’. But their criticism did not particularly disturb Pauling, who saw the bond strength function giving angular dependence as ‘really pretty good, not perfect but pretty good’.³³

³⁰ In the 1930s, titles of the ‘Heitler–London–Slater–Pauling’ and the ‘Heitler–London–Pauling–Slater’ theory were both used. But it was generally acknowledged that Slater ‘originally’ or ‘first’ developed it; and that Pauling ‘independently’ enunciated it. See Wheland (1934, p. 474) and Van Vleck and Sherman (1935, pp. 198–199).

³¹ R. T. Birge to R. S. Mulliken (18 April 1931), quoted in Gavroglu and Simões (1994, p. 81).

³² For Pauling’s rising fame, see Hager (1995, pp. 159–160).

³³ Interview with Linus Pauling by John L. Heilbron, p. 16, Archive for the History of Quantum Physics, American Philosophical Society Library, Philadelphia.

The simultaneous discovery of hybridisation by Slater and Pauling underscores the diversity of aims and approaches that happened to produce the same result. For Slater, the directional property of valence was a problem he encountered in his quest to apply the determinantal method to atoms, metals, and molecules; so he was more interested in setting up the general computational scheme than in solving particular cases. For Pauling, however, the spatial arrangement of valence was a problem he grappled with in his search for the nature of the chemical bond; so he was more concerned with explaining various molecular and crystal structures than giving a lengthy, mathematical justification for his treatment. What the two men had in common was the use of quantum mechanics; and yet they used it quite differently. Slater tried to derive results from the first principles of quantum mechanics, and was always rigorous about making approximations. In contrast, Pauling set up his interpretative scheme with rules, which, though based on quantum mechanical studies of diatomic molecules, were devised for handling polyatomic molecules. Where Slater found that physics could solve a chemical problem, Pauling saw that chemistry could discover a useful idea in physics. Slater's audience was the physicists who were interested in exploring chemical problems; Pauling's audience was the chemists who sought to appropriate physical ideas. The two scientists worked on the same problem in different contexts and for different audiences.

Simultaneous discovery often spawns the debate over priority, and the ways in which this debate is contested and resolved allow the sociological analysis of the functions of a scientific community. Robert K. Merton has examined a number of cases from this perspective, pinpointing pathologies of the reward system in science.³⁴ But simultaneous discovery also sheds light on the complexity of the context for the borderland where two or more disciplines overlap. As Thomas S. Kuhn has suggested, simultaneity attests to the coexistence of the broad, interdisciplinary context and the individual, disciplinary context. In the case of hybridisation, the arrival of quantum mechanics constituted a common context for Slater and Pauling to examine the directional property of valence, but their investigative pathways were largely determined by individual commitments and interests. Around 1930, Slater and Pauling both explored a new territory opened between physics and chemistry, the territory later known as chemical physics or quantum chemistry, but their diverse approaches and goals also revealed the persisting gulf between the two traditional disciplines.

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³⁴ See Merton (1973), especially articles entitled 'Priorities in Scientific Discovery', pp. 286–324; 'Singletons and Multiples in Science', pp. 343–370; 'Multiple Discoveries as Strategic Research Site', pp. 371–382; and 'The Matthew Effect in Science', pp. 439–459.

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