Twenty-Five Years of Sanibel Symposia: A Brief Historic and Scientific Survey

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This paper is dedicated to the memory of the late
Professor John Clark Slater,
a great physicist and an
outstanding human being

Let me start by dedicating this lecture to the memory of Professor John Clark Slater, who has meant so much for the development of atomic, molecular, and solid-state theory not only in the United States but all over the world. He was a great physicist and an outstanding human being, and—for more than 15 years—he played an integral part in the Sanibel Symposia.

Some Historical Remarks

Let me next try to answer the question why it all started on Sanibel Island 25 years ago, in January 1961, and I apologize if I must give the story a rather personal touch. In 1948, I had been appointed Docent (Assistant or Associate Professor) in Theoretical Physics at Uppsala University, Uppsala, Sweden; such a position had a duration of six to seven years and could, in principle, not be renewed. Since 1950, I was spending about half of my time each year at various American institutions and, in the Spring of 1955, I tentatively accepted a professorship in the United States, since my appointment in Uppsala was going to be terminated. At this time, I learned that the King of Sweden—H.M.K. Gustaf VI Adolf—offered me the leadership of a new, small research group in the quantum theory of matter at Uppsala University, so—from July 1, 1955—I became the Director of the Uppsala Quantum Chemistry Group with a position at the Swedish Natural Science Research Council. Fortunately, my contact with the United States continued, and I got several Americans as Visiting Professors in Uppsala.

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Together with Professor Harrison Shull—now Chancellor of the University of Colorado in Boulder, Colorado—I discovered that many of the fundamental results in quantum theory from the golden years, 1925–1930, were being forgotten, and that something drastic had to be done to prevent the field from deteriorating. For this purpose, an International Summer Institute in Quantum Chemistry was arranged in Vålådalen in the Swedish mountains for four weeks in 1958—with 30 students and 13 lecturers—followed by a one-week international symposium with Professors Robert S. Mulliken and Linus Pauling as main combatants. I will make some comments about this symposium later. The symposium proceedings were published as "Acta Vålådalensia No. 3"—since the Acta Vålådalensia Nos. 1 and 2 were jocular issues intended to keep up the spirits of the participants in the isolation of the Swedish mountains, no library has ever been able to collect the complete series, in spite of considerable efforts.

The 1958 Summer Institute was so successful that it was decided to try to arrange a considerably larger institute in 1959 at Skogshem, Lidingö, outside Stockholm. The 1959 Institute was a four-week affair with two sessions in parallel—a more elementary part and an advanced part—and it gathered more than 120 participants from more than 20 nations. It was supported by Uppsala University, by the Swedish Natural Science Research Council, and by the US National Science Foundation.

On the suggestion of NSF, I had, in 1958–1959, started considering the possibility of whether the Uppsala group could start a daughter-project somewhere in the United States devoted to the research in the quantum theory of matter and to teaching on research level, and, during my lecture tours, I had the opportunity to look at many different places. It was finally decided the new project should be started at the University of Florida—partly because Gainesville, Florida, was a beautiful, small, garden city, where one could get to work in almost no time, but mainly because the university had a very vigorous administration with President J. Wayne Reitz, Dean of Academic Affairs Robert B. Mautz, Dean of the Graduate School Linton E. Grinter, Chairman of the Chemistry Department Harry H. Sisler, and Chairman of the Physics Department Stanley S. Ballard in charge. You will meet them all at the 25th Anniversary Banquet.

The Florida Quantum Theory Project was formally started on January 1, 1960, and, in addition to me and my family, there arrived several young scientists from Uppsala for their first international assignment: Jan Linderberg with wife, Jean-Louis Calais, and Klaus Appel with wife—the two former pioneers are here today. The second bunch of Uppsala representatives included Yngve Öhrn and Jan Nordling—both with families—and they are represented here today. Since one of the ideas behind the Florida projects was to arrange a four to five week Winter Institute in Quantum Chemistry to be supported by NSF, my wife Karin and I toured the Florida coastline in the spring break of 1960 looking for some beautiful and isolated places, and we looked particularly at Key Biscayne, Flamingo, and Sanibel Island. In these days, Sanibel Island could only be reached by ferry or by small airplanes, so it seemed ideal for our purpose. We hence started negotiations with Mr. Howard Dayton, owner of Casa Ybel Hotel—not knowing that many features of the island would be changed by Hurricane Donna, which occurred in the beginning of the Fall 1960.

The first Winter Institute in Quantum Chemistry and Solid-State Physics at the

University of Florida started December 6, 1960 with three weeks in Gainesville, two weeks on Sanibel Island, followed by a one-week international symposium on the island in January 1961. The number of participants was fairly limited (60–80), whereas the average academic level was comparatively high—around the associate-professor-level. The institutes were supported by the National Science Foundation for many years to come (until this type of grant was legally terminated by the Congress), and I remember particularly that the NSF per diem was $12 per day and participant, which corresponds rather well to the $50 Florida per diem of today. The Sanibel Symposia were, for many years, financially supported by the USAF Office of Scientific Research, which had some form of "monopoly" on this sponsorship. Later, IBM started supporting the part devoted to the Computational Quantum Sciences. There are quite a few of the pioneers from 1961 here today, and I greet them particularly welcome.

One of the ideas behind establishing the new project in Florida was that we should try to establish contact with the major universities in Latin America: Mexico, Brazil, Argentina, Chile, etc., and we were happy to see that these efforts were successful and of essential importance for the development of quantum sciences on this continent.

The Florida Winter Institutes ended in 1972 due to lack of support, whereas the Uppsala Summer Institutes were still being arranged in a new form in 1984.

The Sanibel Symposia are still going strong, and by now it is clear that more than 5000 scientists representing more than 40 nations have attended these symposia. Professor John C. Slater never came to the 1961 Sanibel Symposium. In a letter to me he wrote, "I will be happy to participate in these symposia, whenever you arrange them in a place which I can easily reach by air from Boston. Sanibel Island seems to be situated out of this world." A couple of years later, Dr. Slater made a special effort and came to a Sanibel Symposium. He and his wife, Rose, fell in love with the primitive beauty of the island, and a few years later, they built their own house not too far from the lighthouse. They became an integral part of the Sanibel Symposia. Dr. Slater finally died on the island (July 25, 1976).

One of the great pioneers in quantum theory and its applications from the golden years, 1925–1930, was Professor Egil Hylleraas, Oslo University, Oslo, Norway, and Harrison Shull and I had convinced him that he should reprint his collected papers, so that they would be easily available to the new generation of quantum scientists. In 1963, we arranged a special Sanibel Symposium in his honor and it turned out to be a fine international gathering with the proceedings published in *Reviews of Modern Physics*. The 1965 Symposium was honoring Professor Robert S. Mulliken of the University of Chicago, with the proceeding published as a separate issue of the *Journal of Chemical Physics*. By now, the American Institute of Physics seemed worried that we were trying to take over part of their publication activities, so we finally decided that we would publish the Sanibel Proceedings in our own journal—the *International Journal of Quantum Chemistry*, to be published by the Interscience Division of John Wiley and Sons, New York—with the first issue appearing January 1, 1967, and editorial offices in the Uppsala group and in the Florida project.

The odd-year honorary symposia continued, and the series contains the names of many of the famous pioneers in the quantum sciences:

1963: E. Hylleraas	1977: L. Pauling
1965: R.S. Mulliken	1979: A. Einstein 100th Anniversary
1967: J.C. Slater	1980: E. Bright Wilson
1969: H. Eyring	1982: J.E. Mayer
1971: J.H. Van Vleck	1983: Sir David Bates
1973: E.U. Condon	1984: M. Kotani
1975: L.H. Thomas	

From the very beginning, one day of the Sanibel Symposia had always been devoted to Quantum Biology, and Professors Alberte and Bernard Pullman, Paris, have been the leaders of these activities over all the 25 years. In 1974, it was finally decided that Quantum Biology should have its own three-day symposium, and this is still the arrangement. Even in this series, there have been special honorary symposia:

1976: A. Szent-Gyorgyi
1979: A. and B. Pullman

devoted to the pioneers in this field.

It was realized that the building of the causeway to Sanibel Island in the late 1960s would successively change its structure, and that the island would gradually lose much of its primitive charm. The scientists joined the islanders in their efforts to try to prevent the building of high-rise condominia, and, even if the builders were finally winning the battle, it should probably be admitted that most of the condominia along the Sanibel shoreline are built in very good taste. However, with this enormous development in real estate, the number of cars on the island increased to such an extent that the traffic was almost always jammed, and it became difficult to get to and from the airport. In 1976, the bulldozers started to take away the old buildings at Casa Ybel, and, even if the condominia still offered an alternative, it was finally decided to leave the island.

In 1977, the Sanibel Symposia were for the first time arranged on Florida's east coast—at the Sheraton Palm Coast Resort Inn about 30 miles south of St. Augustine. For eight years, the Sheraton provided a new ideal environment for the Sanibel Symposia. In 1985, the organizers had the intention of returning to Sanibel Island for the 25th anniversary of the symposia, but this proved not to be possible. Since further the Sheraton had sold out our original dates, we decided that we had to look for a completely new place. As a result, we are celebrating the 25th Anniversary of the Sanibel Symposia at the Whitney Marine Biological Laboratory of the University of Florida at Marineland, with the participants accommodated at the Marineland Quality Inn, and I am convinced that you will all find that this was a most satisfactory solution.

Before going into the discussion of the various scientific topics treated at the Sanibel Symposia, I would like to say a few words about the general philosophy of these meetings. For this purpose, I would like to go back to a little diagram I first showed at the Vålådalen Symposium in the Swedish mountains in 1958. On the horizontal axis is indicated the refinement of the theory, and on the vertical axis the agreement between theory and experiment. As the theory is developed in terms of simple concepts, the

curve approaches a point where there is almost complete agreement between theory and experiment, and—with the kind consent of Professor Linus Pauling—this point was called the "Pauling point." However, one can always improve the theory—and suddenly the good agreement is gone, and one is approaching a minimum, which could perhaps be called the "Ph.D. point." From then on, the curve starts rising again—hopefully in the asymptotic limit approaching the line of perfect agreement between theory and experiment.
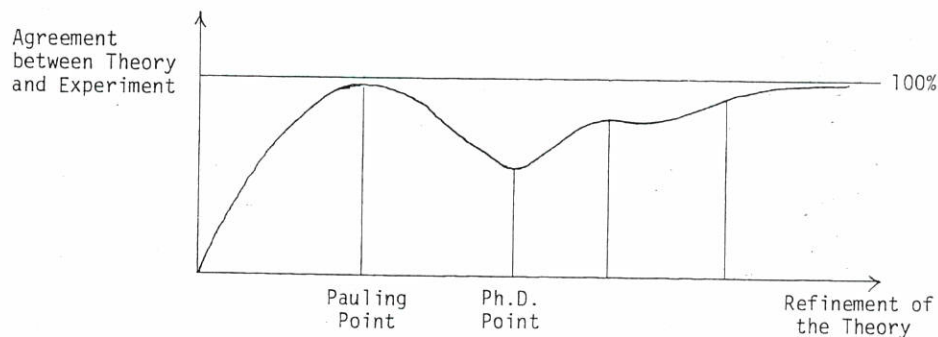
There are many examples of this phenomenon, particularly from the early 1930s. In the theory of the chemical bonding of conjugated systems, or in solid-state theory, one could often get excellent results if one neglected the overlap between the atomic orbitals involved. The results would be changed, however, if one included the so-called overlap integrals, and, in solid-state theory, one would have a real "nonorthogonality catastrophe."

In inorganic chemistry, the crystal field theory was finally a great success until one tried to improve it by including the details of the ligands and to formulate it as a "ligand field theory."

Thanks to the developments of the electronic computers, most applications of the theory to small systems have today successfully passed the first maxima and minima on the agreement-curve. However, when it comes to more complicated systems, it is still interesting to find out where the results belong on the agreement curve.

Most modern graduate students have probably learned that there is no reason for their thesis results to stop at the "Ph.D. point," since there is often a senior faculty member around who is willing to give the lecture, "How to Get Good Results without Actually Cheating." Mathematics is apparently flexible enough to permit us to explain known experimental results—the essential problem of the theory is then to *predict* experimental results which are still unknown.

The main point of this discussion is that good agreement between theory and experiment is a necessary—but by no means sufficient criterion for the goodness of a theory. The main aim of the Sanibel Symposia has always been to go beyond the "Pauling point" and to really test the final outcome of the theory. There is no question that this is also the main goal today.

Some Scientific Aspects

In looking back over 25 years of Sanibel Symposia, it becomes evident that the scientific emphasis of the symposia has shifted a great deal over the years. This has partly been due to planning from the side of the organizers and partly dependent on the fact that some of the plenary lecturers have delivered some real surprises.

The 1961 Symposium was devoted to a general survey of atomic, molecular, and solid-state physics with a great deal of emphasis on the Hartree–Fock scheme and to its extension by the CI-method. The 1963 Hylleraas symposium was considerably more advanced with emphasis on the correlation problem associated with the Coulomb repulsion— e^2/r_{12} —on the representability problem for the reduced density matrices, and on the symmetry dilemma in the restricted variational methods (like Hartree–Fock).

Let us start by reviewing some results related to reduced density matrices. In general quantum statistics, a system of N electrons is described by a system operator Γ having the properties

$$\Gamma \geq 0, \quad \Gamma^\dagger = \Gamma, \quad \mathrm{Tr}\,\Gamma = 1, \tag{1}$$

whereas all the system operators $\{\Gamma\}$ form a *convex set*. If $\underline{\overline{X}} = \{x_1, x_2, \ldots x_N\}$ is the composite coordinate, the system operator Γ has a kernel:

$$\Gamma(\underline{\overline{X}}|\underline{\overline{X}}') = \Gamma(x_1, x_2, \ldots x_N | x_1', x_2', \ldots x_N') \tag{2}$$

usually referred to as a *density matrix*. For an electronic system, the kernel is antisymmetric in each set of the coordinates. The convex set $\{\Gamma\}$ is determined by its limit points, satisfying the additional relation $\Gamma^2 = \Gamma$, in which case the projector Γ has a range $\{\Psi\alpha\}$ which uniquely defines a normalized "wave function" Ψ, so that $\Gamma = |\Psi\rangle\langle\Psi|$. In such a case, one has a *pure state* in quantum mechanics, and the *density matrices* by successive trace formation; for instance:

$$\Gamma(x_1, x_2, \ldots x_N | x_1', x_2', \ldots x_N') = \Psi(x_1, x_2, \ldots x_N)\, \Psi^*(x_1', x_2', \ldots x_N'). \tag{3}$$

Starting from the Nth order density matrix, one can now define a series of *reduced density matrices* by successive formation; for instance:

$$\Gamma(x_1, x_2, \ldots x_p | x_1', x_2', \ldots x_p')$$

$$= \binom{N}{p} \int \Gamma(x_1, x_2, \ldots x_p, x_{p+1} \ldots x_N | x_1', x_2', \ldots x_p', x_{p+1}, \ldots x_N)\, dx_{p+1} \ldots dx_N, \tag{4}$$

$$\Gamma(x_1, x_2 | x_1', x_2')$$

$$= \binom{N}{2} \int \Gamma(x_1, x_2, x_3, \ldots x_N | x_1', x_2', x_3, \ldots x_N)\, dx_3 \ldots dx_N, \tag{5}$$

$$\Gamma(x_1 | x_1')$$

$$= N \int \Gamma(x_1, x_2, \ldots x_N | x_1', x_2 \ldots x_N)\, dx_2 \ldots dx_N. \tag{6}$$

By considering the spectral resolution of the first-order density matrix:

$$\Gamma(x_1|x_1') = \sum_k n_k X_k(x_1) X_k^*(x_1'), \tag{7}$$

one gets the *natural spin-orbitals* $X_k(x_1)$, and by studying the spectral resolution of the second-order density matrix

$$\Gamma(x_1,x_2|x_1',x_2') = \sum_k m_k X_k(x_1,x_2) X_k^*(x_1',x_2'), \tag{8}$$

one obtains the *natural geminals* $X_k(x_1,x_2)$.

Using the reduced density matrices, we will now discuss the *correlation problem* connected with the Coulomb repulsion e^2/r_{12}. For the total electronic Coulomb energy, one has the expression:

$$C = e^2 \int \int \frac{\Gamma(x_1x_2|x_1x_2)}{r_{12}} \, dx_1 \, dx_2 . \tag{9}$$

Since the reduced second-order density matrix $\Gamma(x_1x_2|x_1'x_2')$ is antisymmetric in each set of its indices, so that

$$\Gamma(x_2,x_1|x_1',x_2') = -\Gamma(x_1,x_2|x_1',x_2') = \Gamma(x_1,x_2|x_2',x_1') \tag{10}$$

one has

$$\Gamma(x_1,x_2|x_1',x_2') = 0, \tag{11}$$

for $x_1 = x_2$ and $x_1' = x_2'$, or $r_{12} = 0$ and $\zeta_1 = \zeta_2$, which is the famous "Fermi hole" for parallel spins. The correlation problem is connected with the fact that, for antiparallel spins $\zeta_1 \neq \zeta_2$, one needs a "Coulomb hole" of the form

$$\Gamma(x_1,x_2|x_1',x_2') \approx 0, \tag{12}$$

whenever $r_1 = r_2$, i.e., $r_{12} = 0$. A great deal of time at the 1963 conference was devoted to discussions of the shape of the Coulomb hole, and to the proper treatment of the correlation problem—particularly since this was one of Professor Hylleraas' specialities.

Let us next turn to the *representability problem* for the reduced density matrices. In non-relativistic atomic, molecular, or solid-state theory with fixed nuclei, the Hamiltonian takes the form:

$$H = H_{(0)} + \sum_i H_i + \sum_{i<j} H_{ij}, \tag{13}$$

where $H_{(0)}$ is the nuclear Coulomb repulsion energy, H_i is the sum of the kinetic energy of electron i and its Coulomb attraction energy in the field of the nuclei, and H_{ij} is the interelectronic Coulomb repulsion energy e^2/r_{ij}. For the expectation value of the Hamiltonian, one obtains

$$\langle H \rangle = \mathrm{Tr} H \Gamma = H_{(0)} + \int H_1 \Gamma(x_1|x_1') \, dx_1 + \int H_{12} \Gamma(x_1,x_2|x_1',x_2') \, dx_1 \, dx_2, \tag{14}$$

where the operators H_1 and H_{12} in the integrands work only on the unprimed coordinates, and one puts $x_1' = x_1$ and $x_2' = x_2$ before the integrations are carried out. Using the connections between the density matrices, one may write

$$\langle H \rangle = \int K_{12} \Gamma(x_1, x_2 | x_1', x_2') \, dx_1 \, dx_2 \qquad (15)$$

where

$$K_{12} = \frac{2}{N(N-1)} H_0 + \frac{1}{N-1} \{H_1 + H_2\} + H_{12}, \qquad (16)$$

is the *reduced two-particle Hamiltonian* studied, e.g., by A.J. Coleman. It is easily shown that, if the N-electron system has a ground state with the energy E_0, and the Nth order density matrix satisfies the relations (1), then one has the inequality

$$\langle H \rangle \geq E_0, \qquad (17)$$

which may form the basis for a variational principle. The expressions (14) and (15) depend only on the second-order density matrix $\Gamma(x_1, x_2 | x_1', x_2')$, and such a density matrix is said to be *ensemble-representable* if it may be derived from a Nth order density matrix satisfying the relations (1) by means of the formula (5). Such a density matrix is said to be *wave-function representable*, if the Nth order density matrix may be written in the special form (3). There have been numerous necessary conditions given for the representability of a second-order density matrix, whereas it has been very difficult to give some sufficient conditions—short of solving the Schrödinger equation itself. At the 1963 conference a great deal of time and effort were devoted to the representability problem.

In this connection, Coleman also studied antisymmetric wavefunctions, which were built up by antisymmetrized geminal powers (AGP):

$$\Psi(x_1, x_2, x_3, \ldots x_{2n}) = (N!)^{-1} \sum_p (-1)^p \, P g(x_1, x_2) \ldots g(x_{2n-1}, x_{2n})$$

$$= O_{AS} \prod_{k=1}^{n} g(x_{2k-1}, x_{2k}), \qquad (18)$$

and proved not only that they contain the Hartree–Fock approximation as a special case, but also that they go far beyond this approximation in treating the correlation problem.

At the 1963 symposium, one also discussed the *symmetry dilemma* in the Hartree–Fock method and similar restricted variational treatments. Let us assume that the Hamiltonian H has a constant of motion Q, which is also a self-adjoint projector, so that

$$HQ = QH, \quad Q^2 = Q, \quad Q^\dagger = Q. \qquad (19)$$

In such a case, it is easily shown that, if Ψ is an exact eigenfunction to H, so that

$$H\Psi = E\Psi, \tag{20}$$

then one has

$$Q\Psi = \Psi, \tag{21}$$

either by necessity in the nondegenerate case or by choice in the degenerate case. This theorem implies that, if the Hamiltonian H has a specific symmetry property, then the exact eigenfunctions will be automatically symmetry-adapted or may be arranged in that way.

In the Hartree–Fock method, the total wavefunction Ψ is approximated by a single Slater determinant D, so that $\Psi \approx D$. Starting from the expectation value

$$\langle H \rangle = \frac{\langle D|H|D \rangle}{\langle D|D \rangle}, \tag{22}$$

one determines the best determinant D by means of the variation principle $\delta\langle H \rangle = 0$, which leads to the famous Hartree–Fock equations. The *symmetry dilemma* arises from the fact that one has overlooked that the *approximate* wavefunction D does not automatically satisfy relation (21) or:

$$QD = D. \tag{23}$$

In fact, the relation represents a *variational constant* which will raise the energy. It is interesting to observe that, if one introduces the condition (23) in the beginning of a self-consistent-field cycle, it remains self-consistent and leads to a symmetry-adapted Slater determinant D corresponding to a local minimum. On the other hand, if one gives up the constraint (23), the solution of the Hartree–Fock equations may lead to an *absolute minimum* for the expectation value $\langle H \rangle$, which is usually no longer symmetry-adapted, i.e., $QD \neq D$.

If the constraint $QD = D$ is imposed, one speaks of the Restricted Hartree–Fock (RHF) method, otherwise of the Unrestricted Hartree–Fock (UHF) method. The discovery of the symmetry dilemma led immediately to a deeper insight into the connection between the various Hartree–Fock schemes, and to a new understanding of the phenomena of spin-polarization and correlation splitting of orbitals. At the following Sanibel Symposia, a large number of examples of not symmetry-adapted absolute minima were demonstrated.

Today we would perhaps say that the absolute minimum of $\langle H \rangle$ would correspond to the General Hartree–Fock (GHF) method, and note that the mathematical existence of the corresponding solutions has been proven by B. Simon and E. Lieb, even if—so far—no one has evaluated them in practice. It is interesting to observe that the mathematical existence of the solutions to the RHF scheme has not yet been established, whereas these solutions have been evaluated in practice in many different cases. This provides an excellent example of the mathematical dilemma in many areas of modern theoretical physics and chemistry.

At the 1965 Mulliken Symposium, it is clear that a great deal of attention was

devoted to the *molecular-orbital* (MO) methods in general, and to the ASP-MO-LCAO-SCF methods in particular. The developments in these areas—for which Robert S. Mulliken was awarded the 1966 Nobel Prize in Chemistry—are well-known and do not need an explicit presentation here.

Instead we will briefly comment on the calculation of *lower bounds* to energy eigenvalues by means of a *truncated* basis—a fact which turned out to be a great surprise to most of the participants. If A is a positive definite self-adjoint operator with the inverse A^{-1}, and $h = \{h_1, h_2, \ldots h_p\}$ is a linearly independent set of order p, and $\Delta = \langle h | A^{-1} | h \rangle$ is a quadratic matrix of order $p \times p$ with the inverse matrix $d = \Delta^{-1}$, then it is easily shown that the operator

$$A' = |h\rangle \langle h | A^{-1} | h \rangle^{-1} \langle h | = \sum_{k,l=1}^{p} |h_k\rangle \, d_{kl} \, \langle h_l| , \tag{24}$$

is a *lower bound* to the operator A and approaches it from below when $p \to \infty$, and the set h becomes complete. The operator A' is often referred to as an *inner projection* of the operator A, and it should be observed that the lower-bound property may be extended also to operators which are not positive definite, as long as the negative part is finite. If $H = H_0 + V$ is a perturbed Hamiltonian, where V is a positive definite perturbation, then $H' = H_0 + V'$ is a lower bound to H. For the associated eigenvalues, one has

$$E_k' < E_k, \tag{25}$$

in order from below, which leads to a simple method for calculating lower bounds to eigenvalues with whatever accuracy is desired. A series of papers on lower bounds was presented at this meeting by the various members of the Florida Quantum Theory Project covering such applications as the He-like ions, the rigid rotator, the anharmonic oscillator, the double-well potentials, and the low-lying excited states of He and H^-.

At the 1967 Slater Symposium, a great deal of attention was devoted to the exchange-correlation effects, the $\overline{X}_\alpha$-method, and the applications to solid-state physics. In the Hartree–Fock scheme, the so-called effective Hamiltonian takes the form:

$$H_{\text{eff}}(1) = \frac{p_1^2}{2m} - e^2 \sum_g \frac{Z_g}{r_{1g}} + e^2 \int dx_2 \, \frac{\rho(x_2,x_2) - \rho(x_1,x_2) \, P_{12}}{r_{12}} , \tag{26}$$

and of particular importance is the "exchange term":

$$V_{\text{exch}}(1) = -e^2 \int dx_2 \, \frac{\rho(x_1,x_2) \, P_{12}}{r_{12}} , \tag{27}$$

where P_{12} is the permutation operator defined through the relation $P_{12} f(x_1,x_2) = f(x_2,x_1)$. The exchange term is a rather complicated, nonlocal potential, and we note that already in the 1930s in the Thomas–Fermi–Dirac theory, the following approximation had been suggested:

$$V_{X\alpha}(1) = -6\alpha \, (3\rho/8\pi)^{1/3}. \tag{28}$$

This approximate form was taken up again in 1951 by Slater who suggested the value $\alpha = 1$. It was shown by Gaspar that $\alpha = \frac{2}{3}$ would lead to a better approximation, and

this value was also used by Kohn and Sham in 1965.

The formula (28) forms the basis for Slater's $\overline{X}$-alpha method, which combined with the augmented plane wave (APW) method, turned out to be an excellent tool for studies in applied solid-state theory. Slater could now study many complicated crystals under normal conditions or under very high pressure, and he could investigate their ferromagnetic or anti-ferromagnetic properties. A long-time dream as to applications started to become a reality.

In the APW method, it became customary to use the muffin-tin approximation and to introduce the proper non-muffin-tin corrections—a problem which has got its proper solution only during the last few years. The entire approach was enormously successful as carried out by J. Connolly, K. Johnson, D. Ellis, A. Freeman, and other Slater associates. The $\overline{X}_\alpha$-method and its applications to solids was going to be a standard part of the Sanibel Symposia for almost a decade to come, and Professor John C. Slater loved to gather his students, postdoctoral fellows, associates, and professors for a special meeting outside the lecture hall in one of the afternoons to listen to the recent progress reports from other institutions.

At the 1967 symposium, the very last lecture was given for the first time by Professor Berndt Matthias from the University of California in La Jolla and Bell Telephone Laboratories, who spoke about the superconducting properties of new alloys and predicted what elements would be found to be superconducting in the year to come. This started a long tradition at the Sanibel Symposia, which was only broken when Berndt passed away in 1980. In his lecture, Berndt often made fun of the theoreticians in connection with their complicated attempts to explain superconductivity, but he sometimes needled also the experimentalists and the various claims as to the discovery of high-temperature superconductors. In his predictions, he was always correct—probably because he had already gathered enough unpublished experimental results himself. His presence added a great deal of "intellectual spice" to a long series of Sanibel Symposia.

Personally, I felt that even with Professor Slater's enormous success in the solid-state applications, there were new elements in solid-state physics which should not be neglected at the Sanibel Symposia, e.g., the new developments in spin-wave and charge-wave theory. Professor Slater responded to these ideas by finishing his own lecture with an anecdote about an old Quaker couple sitting meditating together. "The old man said, 'I thought we had agreed that the whole world is crazy, except for thee and me—and now I start wondering about thee,' " said Professor Slater and looked at me. But Professor Slater had a generous nature, and Professor Al Overhauser was invited to speak about the new developments at a following Sanibel Symposium.

The $\overline{X}_\alpha$-method is a simple example of a "density functional method," in which a complicated nonlocal potential is approximated by a potential, which depends on the electron density ρ only. According to the Hohenberg–Kohn theorem from the 1960s, the ground state energy of any atomic, molecular, or solid-state system with fixed nuclei is a unique *functional* of the electron density ρ:

$$E = E(\rho). \tag{29}$$

If we go back and remember the problem one has to show whether a second-order

reduced density matrix $\Gamma = \Gamma(x_1 x_2 | x_1' x_2')$ is representable or not, we realize how difficult it must be to describe a system using only the electron density:

$$\rho(x_1) = \Gamma(x_1 | x_1) = \frac{2}{N-1} \int \Gamma(x_1 x_2 | x_1 x_2) \, dx_2. \tag{30}$$

However, Professor E. Bright Wilson has given the following interpretation of this rather difficult situation: if one knows ρ, one knows also the total number of electrons, since $\mathrm{Tr}\rho = N$; the cusps of ρ will further indicate the locations of the nuclei, and the shape of the cusps will give the atomic numbers of the nuclei involved. Hence, one can construct the N-electron Schrödinger equation for fixed nuclei, and the solution determines all the electronic properties including the ground-state energy. This gives undoubtedly an explicit recipe for the Hohenberg–Kohn functional, and we note that it gives also a solution to the problem of whether a given second-order density matrix $\Gamma(x_1 x_2 | x_1' x_2')$ is wave-function representable or not. For some reason, the Bright–Wilson interpretation does not seem to be popular among the practitioners in these areas. As we will see, the density-functional methods play a very important role also at the current Sanibel Symposia.

In treating complicated systems, the *semi-empirical methods* have been of fundamental importance in many of the Sanibel Symposia over the last 25 years. In atomic theory, Slater's theory of atomic spectra based on the F- and G-integrals had been very successful; in molecular theory, the concept of chemical "resonance" developed by Pauling and by Slater had turned out to be very forceful; and, in solid-state theory, the semi-empirical theory of band structure constructed by Bloch, Brillouin, Slater and others, and the crystal field theory developed by Van Vleck had proven to be most useful. Many aspects of these approaches were reviewed at the early Sanibel Symposia, but one usually had considerable difficulties in reaching any improvements—these semi-empirical theories were apparently at their "Pauling points."

The treatment of *conjugated systems* is of particular importance in the study of large biomolecules, and here the semi-empirical methods seemed to provide the only possible approach—especially in the beginning. Everyone here realizes the importance of the Hückel method and the Extended Hückel Theory (EHT) in this connection. In 1953, the Pariser–Parr–Pople (PPP) model represented a forceful attempt to take also certain correlation effects into account, and it led to the concept of the "Neglect of Differential Overlap" (NDO), which even today appears in such well-known symbols as CNDO (introduced by John Pople at Sanibel in 1965), INDO, MINDO, NDDO, etc. In the author's opinion, part of the success of the PPP-model may be explained if one replaces the original atomic orbitals (AO's) ϕ by the orthonormalized atomic orbitals (ONAO's) φ obtained by the symmetric ortho-normalization:

$$\varphi = \phi \langle \phi | \phi \rangle^{-1/2}; \tag{31}$$

these aspects have been further developed by Ohno and by Fischer–Hjalmars.

Even if the semi-empirical theories are highly useful, they are often characterized by the dilemma that they are brought to a certain "Pauling point" beyond which they cannot be improved. The theory itself may contain hundreds of parameters to be

determined by a few experimental data, and, in this situation, one often assumes that only a few theoretical parameters are of importance and that all others are negligible. This leads often to the disappointing result that, once these parameters are calculated on a pure theoretical basis, the values usually differ considerably from those obtained from the experimental data. It is evident that the semi-empirical theories ought to be improved, but we still don't know how.

The *ab-initio methods* for treating atomic, molecular, and solid-state systems are based on the idea that the systems are essentially described by the *atomic numbers Z_g* of the atomic nuclei involved, and that these nuclei in the Born–Oppenheimer approximation may be considered as fixed. In such a case, one knows the nonrelativistic Hamiltonian H, and the main problem is to solve the time-dependent Schrödinger equation

$$- \frac{h}{2\pi i} \frac{\partial \Psi}{\partial t} = H\Psi, \tag{32}$$

or the associated eigenvalue problem:

$$H\Psi = E\Psi, \tag{33}$$

for the ground state and the low-lying excited states. It should be observed that, even if one today has a great deal of experience in treating different symmetries and various types of nuclear "conformations," one has had considerable difficulties in going beyond the Born–Oppenheimer approximation, and that much work remains to be done.

For small and moderate-size systems, the various *Hartree–Fock methods* (RHF, UHF, PHF, etc.) have now become standard and the author is only disappointed that the general Projected-Hartree–Fock (PHF) method has not been more frequently applied; in the treatment of conjugated systems and in the study of band theory, it is used essentially in a special form called the alternant-molecular-orbital (AMO) method. Even the MC-SCF methods have become standard, but the most essential developments have appeared in the method of *superposition of configurations* or configurational interaction (CI) approach, to use an historical term.

Already in the 1930s, it was pointed out by P. Jordan that the structure of the CI-expansion may be understood and simplified by using the properties of the unitary group. The irreducible representations of the unitary group were later classified by Gelfand, and the so-called Gelfand symbols became an important tool in many parts of theoretical physics. In the 1960s, several quantum chemists (Linderberg and Öhrn, Matsen, Paldus, and Cizek, and others) discovered the usefulness of the Unitary Group Approach (UGA), and by means of the Gelfand symbols, the theory was put in a graphical form (Shavitt, Siegbahn, etc.) and simplified so that one could finally handle wave functions containing more than one million configurations (Handy). The various forms of UGA have played an essential role at the Sanibel Symposia, and many of the pioneers in this field are here today.

The effectiveness of the CI-expansions depends to a large extent on the choice of the basis sets, and today the *Gaussians* still play a dominating role in the applications. Unfortunately, the Gaussians can never express the correct asymptotic form of the atomic and molecular wavefunctions, and this approach must then necessarily have a

rather limited applicability. Authors interested in the correct asymptotic behavior have often preferred to use *Slater-type orbitals* (STOs) and, during the last decade, there has been a renewed interest in the expansion of STOs on one atomic center around another center in terms of the so-called alpha-functions, which are useful in the evaluation of two-, three-, and four-center integrals.

There is no question that the CI-methods are fairly primitive and that their success depends on the existence of "number crunchers"; in fact, they have greatly benefitted by the development of the electronic computers: from the scalar computers to vector computers, to supercomputers. Today almost every quantum scientist wants a supercomputer, and, in this connection, I would like to quote a saying by Peter Debye at the 1955 Texas Conference about computers in general: "If you have them—use them; if you don't have them—beat them!"

Let me confess that I think that the computers have added a great deal to the Sanibel Symposia over the years, not only in the form of numbers—which are sometimes difficult to understand—but particularly in the form of "computer graphics" which have turned out to have a special appeal to the "chemists" in us, and which has provided a new visual understanding of an otherwise very abstract field.

The big question is, of course, whether one can beat the CI-methods and the number crunchers by a more conceptual approach to our field based more on ideas than on "brute force." The Sanibel Symposia have seen many developments of this type which I will summarize under the name of *wave operator methods*. In this case, one starts from a normalized *reference function* φ, and one expresses the solution Ψ to the eigenvalue problem (33) in the form

$$\Psi = W\varphi, \tag{34}$$

where W is the wave operator, which is by no means unique. One usually requires that the eigenfunction Ψ satisfies the *intermediate normalization*:

$$\langle \varphi | \Psi \rangle = \langle \varphi | W | \varphi \rangle = 1, \tag{35}$$

which has the advantage that it is applicable both to the discrete states and to the continuum.

The wave operator approach has reflected the tremendous development in *perturbation theory* over the last few decades, and a rather thorough survey was given at the 1978 Sanibel Workshop on "large-order perturbation theory."

Another forceful approach has been provided by the *resolvent methods*, which are sometimes referred to as propagator methods or Greens-function techniques. If z is a complex variable, the resolvent $R(z)$ to the Hamiltonian is defined through the relation

$$R(z) = (z \cdot 1 - H)^{-1} \tag{36}$$

which is well-defined for $z \neq E$. In mathematics, the spectrum $\{E\}$ for the Hamiltonian H is customarily defined as the complement to the set for which the resolvent is regular. It should be observed that, even if the Hamiltonian is an unbounded operator, the resolvent is usually *bounded*: if $|z - E| \geq \rho$, one has

$$\parallel R\Phi \parallel \ \leq \frac{1}{\rho} \ \parallel \Phi \parallel, \tag{37}$$

for any wave function Φ. We note that the Hamiltonian and the resolvent has the same eigenfunctions Ψ:

$$H\Psi = E\Psi, \ R(z)\Psi = r(z)\Psi, \tag{38}$$

and that the eigenvalues are connected through the relations:

$$r(z) = (z - E)^{-1}, \ E = z - r^{-1}. \tag{39}$$

In mathematics, the resolvent was originally as a tool for solving the inhomogeneous equation:

$$(H - z \cdot 1) \ \Psi_z = a\varphi, \tag{40}$$

where the coefficient a may be determined so that the solution Ψ_z satisfies the intermediate normalization (35). Using the resolvent, one gets directly:

$$\Psi_z = -aR(Z)\varphi = \frac{R\varphi}{\langle \varphi | R | \varphi \rangle}, \tag{41}$$

where $a = -\langle \varphi | R | \varphi \rangle^{-1}$ and

$$W(z) = \langle \varphi | R(z) | \varphi \rangle, \tag{42}$$

is the so-called *Weinstein function*, which is a typical example of a Green's function. We note that Eq. (40) goes over into the eigenvalue relation (33) for $a = 0$, and it is easily shown that the eigenvalues $z = E$ associated with the boundary consition (35) will now be represented by *simple poles* in the Weinstein function—even if the eigenvalues themselves are highly degenerate. If one substitutes the expansion formula

$$R(z) \equiv z^{-1} + z^{-1} H R(z), \tag{43}$$

into the Weinstein function, one obtains so-called propagator formulas, which form the basis for the propagator methods.

It should be observed that, even of the poles of the Weinstein function gives the eigenvalues $z = E$, the expression (41) for the wave function takes the form ∞/∞, whenever z approaches an eigenvalue E. In order to carry out this limiting procedure, one may proceed in a slightly different way.

For this purpose, one introduces the projector $O = |\varphi\rangle\langle\varphi|$ as well as the projector $P = 1 - O$ for its complement. One gets directly

$$O\varphi = \varphi, \qquad O\Psi_z = \varphi,$$

$$P\varphi = 0, \qquad P\Psi_z = \Psi_z - \varphi. \tag{44}$$

Letting the operator P work on the imhomogeneous equation (40), one obtains

$$P (H - z \cdot 1)\Psi_z = 0, \tag{45}$$

$$\left(1 - \frac{PH}{z}\right)\Psi_z = \varphi, \tag{46}$$

and

$$\Psi_z = \left(1 - \frac{PH}{z}\right)^{-1} \varphi, \tag{47}$$

which gives an explicit expression for the wave operator:

$$W = \left(1 - \frac{PH}{z}\right)^{-1}. \tag{48}$$

It is evident that, for all values of z including the eigenvalues $z = E$, one has the simple indentity:

$$\Psi_z \equiv \frac{R(z)\varphi}{\langle\varphi|R(z)|\varphi\rangle} \equiv \left(1 - \frac{PH}{z}\right)^{-1} \varphi, \tag{49}$$

which is highly useful in many connections. Formula (47) forms the basis for the so-called *partitioning technique*, which the author has studied in a series of papers.

Multiplying the inhomogeneous equation (40) to the left by $\langle\varphi|$, one obtains:

$$a = \langle\varphi|H - z \cdot 1|\Psi_z\rangle = \langle\varphi|H|\Psi_z\rangle - z$$

$$= \langle\varphi|H \left(1 - \frac{PH}{z}\right)^{-1}|\varphi\rangle - z \equiv f(z) - z, \tag{50}$$

where $f(z)$ is the so-called brecketing function. It is obvious that, instead of looking for the poles of the Weinstein function, one may look for the zero-points of the function

$$a \equiv f(z) - z. \tag{51}$$

We note particularly that even multiple eigenvalues $z = E$ correspond to single roots of this equation.

If one expresses the wave operator W in exponential form

$$W = e^T, \tag{52}$$

and looks for the explicit form of the operator T, one is led to the *coupled-cluster methods* which have played a fundamental role during the last decade of the Sanibel Symposia.

If one expresses the Hamiltonian in the form $H = H_0 + \lambda V$ and substitutes this expression into the wave operator (48), it may be expanded in a power-series in λ which leads to the corresponding perturbation expansion:

$$E = E_0 + \lambda\epsilon_1 + \lambda^2\epsilon_2 + \lambda^3\epsilon_3 + \cdots . \tag{53}$$

It has been realized that, even if this series is convergent, the summation of a few low-order terms may not lead to any meaningful physical or chemical results, since the series is too slowly convergent. The development of modern numerical analysis has indicated that one should instead look for *rational approximations* of the form:

$$E = \frac{a_0 + \lambda a_1 + \lambda^2 a_2 + \cdots + \lambda^m a_m}{b_0 + \lambda b_1 + \lambda^2 b_2 + \cdots + \lambda^n b_n}. \tag{54}$$

A first attempt was made by constructing the *Padé approximants* to the power series (53). One learned quickly, however, that one could construct the rational approximations directly from various forms of the wave operator (48) by using inner projections (24), where the elements of the inverse matrix $d = \Delta^{-1}$ may be expressed as quotients between determinants. It was gratifying to learn that these rational approximations are always convergent, even when the Padé approximants are not, and that they sometimes provide upper and lower bounds for the quantities involved. It is undoubtedly true that much work remains to be done in this particular field, and that the results obtained so far seem greatly promising.

In conclusion, it should be emphasized that, whereas quantum mechanics deals with the properties of *pure states* characterized by a wave function Ψ, the true properties of the electronic structure of matter are described by a *system operator* Γ having the properties (1) and satisfying the time-dependent *Liouville equation*:

$$-\frac{h}{2\pi i} \frac{\partial \Gamma}{\partial t} = H\Gamma - \Gamma H. \tag{55}$$

The kernel ρ of this operator is often referred to as a *density matrix*; see also relation (2). One may write (55) in a form which is analogous to the Schrödinger equation (32), by introducing a superoperator $\hat{L}$ called the Liouvillian defined through the relation

$$\hat{L}T \equiv HT - TH, \tag{56}$$

where T is an arbitrary operator. This gives

$$-\frac{h}{2\pi i} \frac{\partial \Gamma}{\partial t} = \hat{L}\Gamma. \tag{57}$$

It may be shown that, if one introduces a proper binary product $\{A \,|\, B\}$ in the operator space, one may solve the Liouville equation (57) by exactly the same Hilbert-space methods as the Schrödinger equation (32), and that this holds also for the associated eigenvalue problems. The author prefers the classical Hilbert–Schmidt binary product:

$$\{A \,|\, B\} = \mathrm{Tr} A^\dagger B = \sum_{k,l} A_{kl}^* B_{kl}, \tag{58}$$

particularly since it makes the Liouvillian $\hat{L}$ automatically self-adjoint:

$$\{\hat{L}A \,|\, B\} = \mathrm{Tr}\,(HA - AH)^\dagger B = \mathrm{Tr}\,A^\dagger (HB - BH) = \{A \,|\, \hat{L}B\}, \tag{59}$$

but also many other binary products have been suggested in the literature. The eigenvalue problem for the Liouvillian:

$$\hat{L}C = \nu C, \tag{60}$$

has directly the solution

$$C = |\Psi_f\rangle\langle\Psi_i|, \quad \nu = E_f - E_i, \tag{61}$$

i.e., the eigenvalues ν are directly representing the spectral differences. In the transition from the initial state i to the final state f, one may keep the number N of the electrons constant, or one may shift it to $(N-1)$ or $(N+1)$ in order to obtain ionization energies or electron affinities, respectively.

This Green's function approach was first developed in quantum field theory, and—via nuclear physics—it was introduced to quantum chemistry around 1965 by Linderberg and Öhrn to become one of the more powerful methods for applications in atomic, molecular, and solid-state theory to be dealt with at the Sanibel Symposia. It is obvious from our discussion above that the *superresolvent*

$$\hat{R}(z) = (z \cdot \hat{1} - \hat{L})^{-1} \tag{62}$$

should play a key role in this approach. If F is proper *reference operator*, which is normalized so that $\{F|F\} = 1$, the eigenvalues $Z = \nu$ to the Liouvillian $\hat{L}$ will now be represented by the simple poles of the Weinstein function:

$$W(z) = \{F|\hat{R}(z)|F\}, \tag{63}$$

or the more general "Weinstein matrix." If one introduces the expansion identity

$$\hat{R}(z) \equiv z^{-1} \cdot \hat{1} + z^{-1} \hat{L}\,\hat{R}(z), \tag{64}$$

one obtains the propagator formulas which form the basis of the *propagator methods* proven so practically useful in studying the properties of materials.

Instead of solving the eigenvalue problem (62), one may now consider the associated inhomogeneous equation:

$$(\hat{L} - z \cdot \hat{1})\, C_z = aF, \tag{65}$$

where the coefficient a is determined by the auxiliary condition:

$$\{F|C_z\} = 1. \tag{66}$$

This gives directly the solution:

$$C_z = -a\hat{R}(z)F = \frac{\hat{R}F}{\{F|\hat{R}|F\}} \tag{67}$$

where $a = -\{F|\hat{R}|F\}^{-1}$. It is evident that, even in this case, one has an identity of the type (49), or:

$$C_z \equiv \frac{\hat{R}F}{\{F|\hat{R}|F\}} \equiv \left(\hat{1} - \frac{\hat{P}\hat{L}}{z}\right)^{-1} F \qquad (68)$$

where $\hat{P} = \hat{1} - |F\}\{F|$ is the projector for the complement to $\hat{O} = |F\}\{F|$. From this point, the theory for the Liouvillian $\hat{L}$ may be developed in parallel with the theory for the Hamiltonian H.

It is remarkable that the development of the propagator methods for the Liouvillian has renewed the interest in the AGP-function of the type (18), and I am sure that we will hear more about this approach this morning.

In conclusion, I would like to thank the University of Florida, Uppsala University, the federal agencies, and particularly the staff of the Florida Quantum Theory Project—gofers, secretaries, postdoctoral fellows, and professors, and also my wife, Mrs. Karin Löwdin—for the combined efforts which have made 25 years of Sanibel Symposia possible. We hope to continue these symposia also in the future.