

Walter Kohn: Nobel Prize in Chemistry in 1998

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PROFESSOR Walter Kohn was awarded the Nobel Prize in Chemistry in 1998 jointly with Prof. J. Pople. Kohn and Pople were not professional chemists, but their researches led to important breakthroughs in chemical calculations.

Walter Kohn was born in Vienna, Austria, in 1923. His family left Austria before World War II and he finished his school education in England. He obtained BA and MA from Toronto University in Canada. He joined Harvard University, Boston, Massachusetts, USA, as a Junior Fellow and worked with the famous physicist Julian Schwinger for his PhD in the properties of some elementary particles (Schwinger himself got the Nobel Prize in 1965 for his work in quantum electrodynamics).

Kohn's early publications¹ were concerned with the lower bounds to the eigenvalues of the Schrodinger equation and a variational principle for scattering (Kohn's variational principle). Kohn and Borowitz published two papers on the electromagnetic properties of the nucleon and the stress tensor of the electron, but Kohn then stopped working in this area.

He spent two years (1948–1950) in Niels Bohr's institute at Copenhagen, Denmark, and worked with Jost, on finding the forces between particles from scattering data. This 'inverse scattering problem' was important because the nuclear forces were not known and could be studied through experiments by pp and np scattering.

In 1950, Kohn returned to USA and joined the Carnegie Institute of Technology at Pittsburgh and started work in solid state physics. With Rostoker, he developed the Green function method for the band structure calculation in solids; the method is called the KKR method – Korringa, Kohn and Rostoker method – as Korringa had independently suggested the same idea. As high-speed computers became available, the method was widely used with the muffin-tin potential. Around this time Kohn became a regular summer visitor to the Bell Telephone Laboratories and became acquainted with earlier stalwarts in the field of solid state physics – Wigner, Seitz, Bardeen, Shockley and Herring. The transistor had been invented then, and Kohn developed the effective mass theory in the study of shallow donor states in silicon and germanium. He studied the analytic properties of the Bloch states and the question of the closure of the bands in the presence of external electric and magnetic fields. For the electric field, the closure of

an isolated band could be proved; this problem has connection with the subsequent quest for the 'Bloch' oscillator and the Stark ladders in solids. The corresponding magnetic field problem has not been satisfactorily solved in spite of efforts by Wannier, Blount² and others. A very fruitful collaboration between Kohn and Luttinger started at this time; they looked at the quantum transport problem through the quantum density matrix, and Kohn returned to the transport problem later with some students like Woll and Green. The failure of the simple band theory in distinguishing insulators and conductors was known, and he tried to develop a theory of the insulating state with his first student of Indian origin, Ambegaokar.

The mid-fifties saw some important developments in quantum many-body problem by Brueckner, who initiated a detailed study of the perturbation series. In particular the summation of the 'ring diagrams' in high density electron gas by Brueckner and Gell'mann was an important step in solid state physics. Kohn and Luttinger clarified many points in the application of the perturbation series to the calculation of the ground state properties. Brueckner's procedure was to calculate the ground state energy by taking the limit of zero temperature first and then taking the infinite volume or thermodynamic limit:

$$E_0 = \lim_{N \rightarrow \infty, V \rightarrow \infty, N/V = \rho} \lim_{T \rightarrow 0} E_{N, V, T} \quad (1)$$

Kohn and Luttinger produced some 'anomalous diagrams', which suggested that the correct procedure in solid state physics should be:

$$E_0 = \lim_{T \rightarrow 0} \lim_{N \rightarrow \infty, V \rightarrow \infty, N/V = \rho} E_{N, V, T} \quad (2)$$

The anomalous diagrams require, in statistical mechanical terms, the shift of the chemical potential from its non-interacting value to the correct value for the interacting system. In 1960, Kohn moved to La Jolla in the newly established campus of the University of California there.

In the quantum theory of metals, the states occupied by electrons are separated from unoccupied states by a surface called the Fermi surface in momentum space. Its delineation was being done by many experimental techniques. In the Kohn effect, Walter suggested that the image of this surface could be seen as kinks in the phonon dispersion curves obtained in neutron scattering. The predicted effect was experimentally found in neutron studies at the nuclear reactor

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at Chalk River, Canada³. One of the scientists involved in finding the Kohn anomalies in metals was Iyengar, who later became the Chairman of the Indian Atomic Energy Commission. Another important work in the Hartree-Fock stability theory should be mentioned: Overhauser claimed that the conventional starting point of the free electron Fermi sphere was not correct as this was unstable with regard to long range Coulomb forces; Kohn settled the issue by showing that the conventional starting point was correct as far as short range interactions were concerned – the screened interaction between electrons was indeed short-ranged.

I was the second Indian student of Walter Kohn. My thesis work was related to the study of the Fermi surface by positrons and the effective mass of the positron in metals. The Kohn-Majumdar continuity theorem of bound and unbound states in a Fermi gas originated in this work.

From 1964, Kohn started developing the density functional theory⁴, which led to the Nobel Prize. A functional is a quantity which depends not just on the value of a function at a point but on the entire course of the function. The density of a collection of electrons $n(\vec{r})$ is classically and intuitively understood. Chemists would like to have techniques based on density as a basic variable to describe the properties of atoms and molecules. The Thomas-Fermi theory is one such theory which leads to the equation⁴:

$$\frac{5}{3} C_k n(\vec{r})^{2/3} + e^2 \Phi(\vec{r}) + V_{\text{ext}}(\vec{r}) + \lambda = 0. \quad (3)$$

Φ , the Coulomb potential is given by:

$$\Phi(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}'. \quad (4)$$

C_k is a constant; V_{ext} is the potential due to nuclei; and λ is a Lagrange multiplier. The theory was shown by Teller⁵, not to bind atoms into molecules. The best single particle theory, on the other hand, leads to the Hartree-Fock equations for wave functions; the potential is nonlocal; the equations are non-linear integro-differential equations. Slater did produce a local approximation for the nonlocal exchange, but the correlations were left out.

The density functional theory starts with the Hamiltonian:

$$H = T + V_{ee} + \sum_{i=1}^N V_{\text{ext}}(\vec{r}_i), \quad (5)$$

where T is the kinetic energy, and V_{ee} the electron-electron interaction. If $n(\vec{r})$ is the density obtained from some wavefunction, we define a functional $F[n]$:

$$F[n] = \min_{\psi \rightarrow n} \langle \psi | T + V_{ee} | \psi \rangle. \quad (6)$$

The functional is universal – it does not refer to a specific system or to a specific $V_{\text{ext}}(r)$. The density functional theory rests on two theorems on energy E and the ground state energy E_{GS} :

$$E[n] = \int d\vec{r} V_{\text{ext}}(\vec{r})n(\vec{r}) + F[n] \geq E_{\text{GS}}, \quad (7)$$

$$\int d\vec{r} V_{\text{ext}}(\vec{r})n_{\text{GS}}(\vec{r}) + F[n_{\text{GS}}] = E_{\text{GS}}. \quad (8)$$

Some problems in the foundations of the theory were already foreshadowed in Courant and Hilbert⁶: 'the characteristic difficulty of the calculus of variations is that problems which can be meaningfully formulated may not have solutions – because it is not in general possible to choose the domain of admissible functions as a 'compact set' in which a principle of points accumulation is valid'. As far as applications are concerned, there are no problems with eqs (7) and (8).

The Kohn-Sham decomposition – this is a Hartree-like approximation – writes the kinetic energy $T_0[n]$, exchange-correlation energy $E_{\text{xc}}[n]$ separately, and the energy functional is,

$$E[n] = T_0[n] + \int d\vec{r} n(\vec{r}) [V_{\text{ext}}(\vec{r}) + \frac{1}{2}\Phi(\vec{r})] + E_{\text{xc}}[n]. \quad (9)$$

The variational derivative gives,

$$\frac{\delta E[n]}{\delta n(\vec{r})} = \frac{\delta T_0}{\delta n} + V_{\text{ext}} + \Phi(\vec{r}) + \frac{\delta E_{\text{xc}}}{\delta n} = \mu, \quad (10)$$

where the chemical potential μ comes from the total number conservation,

$$N = \int n(\vec{r}) d\vec{r}. \quad (11)$$

We compare this with a system without the mutual Coulomb interaction;

$$\frac{\delta E[n]}{\delta n} = \frac{\delta T_0}{\delta n} + V(\vec{r}) = \mu. \quad (12)$$

The mathematical problems are identical provided,

$$V = V_{\text{ext}} + \Phi(\vec{r}) + \frac{\delta E_{\text{xc}}[n]}{\delta n}. \quad (13)$$

The solution proceeds by solving a Schroedinger equation

$$\left[-\frac{1}{2}\nabla^2 + V\right]\psi_i(\vec{r}) = \varepsilon_i \psi_i(\vec{r}), \quad (14)$$

with density $n(\vec{r})$ given by,

$$n(\vec{r}) = \sum_{i=1}^N |\psi_i(\vec{r})|^2. \quad (15)$$

Note that the kinetic energy is exactly treated unlike in eq. (3). In eq. (13), $V(\vec{r})$ is local if E_{xc} is local. E_{xc} is obtained from many-body theory in some approximation. The scheme improves on the Thomas–Fermi theory insofar as the kinetic energy is concerned; it improves on the Slater formulation by having the correlations in after a fashion. The solution still proceeds through iteration as the potential eq. (13) depends on density, but the computing machinery for the Schroedinger or Hartree–Fock–Slater equations can be used. Fortunately the molecules can be formed now and the chemists can carry on with their intuition about density.

One of the first applications was to improve Bardeen's classic calculation of the surface by Lang and Kohn⁷, the work was greeted with the Buckley prize of the American Physical Society in solid state physics. The third Indian student of Kohn, Bagchi, worked on surface problems of physisorption and chemisorption.

For a while Kohn went back to the problem of insulators and, with Sherrington, worked on excitonic insulators. But the applications of the density functional theory with numerous workers joining in soon forced him to concentrate on the developments in this field.

In 1979, the Institute of Theoretical Physics was established at the campus of University of California, Santa

Barbara, and Kohn was its first Director. It had a small core faculty but would have many visitors at one point of time discussing and working on a particular problem.

Over the years the density functional theory has been extended in many ways by several workers, including some from India. In December 1994, Kohn came to India to deliver a lecture at a winter school in Bangalore on some recent developments in quantum many-body physics, jointly sponsored by Jawaharlal Nehru Centre for Advanced Scientific Research (Bangalore) and S. N. Bose National Centre for Basic Sciences (Calcutta).

1. The complete list of publications of W. Kohn is available in <http://www.physics.ucsb.edu/~kohn/>
2. Wannier, G., *Rev. Mod. Phys.*, 1962, **34**, 645; Blount, E., *Solid State Physics* (eds Seitz, F. and Turnbull, D.), Academic Press, New York, 1962, vol. 13, p. 306.
3. Brockhouse, B. N., Rao, K. R. and Woods, A. D. B., *Phys. Rev. Lett.*, 1961, **7**, 93; Iyengar, P. K., Venkataraman, G., Gameel, Y. H. and Rao, K. R., Proceedings of the Conference on Inelastic Scattering of Neutrons IAEA, Vienna, 1968, p. 195.
4. The density functional theory has been reviewed in several books and articles like; Bamsai, A. S. and Deb, B. M., *Rev. Mod. Phys.*, 1981, **53**, 95; Jones, R. O. and Gunnarson, O., *ibid*, 1989, **61**, 689; Kohn, W., in *Julian Schwinger, The Physicist, The Teacher and The Man* (ed. Jack Ng, Y.), World Scientific, Singapore, 1996, pp. 65–78.
5. Teller, E., *Rev. Mod. Phys.*, 1962, **34**, 645.
6. Courant, R. and Hilbert, D., *Methods of Mathematical Physics*, Interscience Pub. Inc., New York, 1953, vol. 1, chap. 4, p. 173.
7. Lang, N. D., *Solid State Physics* (eds Ehrenreich, H., Seitz, F. and Turnbull, D.), Academic Press, New York, 1973, vol. 28, p. 225.

Received 2 February 1999; accepted 8 February 1999