GOLDEN JUBILEE MEETING OF INDIAN ACADEMY OF SCIENCES, BANGALORE SUMMARIES OF LECTURES DELIVERED.

Symposium on Animal Communication

ON THE COMMUNICATION OF WELL BEING

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THE content of communicatory exchanges may be classified on the basis of the interests of the signaller and the recipient which may be at variance.

Signaller		
True information sought to be transmitted in mutual interest	True information sought to be suppressed	False information sought to be transmitted against the interest of the recipient
α	β	γ
True information sought to be received in mutual interest	True information sought to be received against the interest of the signaller	False information sought to be discounted in the interest of the receipient
Recipient		

As Wiley[1] has argued, the displays would tend to be stereotyped and repetitive, in other words, ritualized where γ is a dominant component, while they are expected to be inconspicuous when β dominates. In cases of mutualism, where α dominates, the signals may be conspicuous when an immediate response is favoured, but rather subtle and variable otherwise. Over 80% of the events of tactile communication that we have noted in our study of the social behaviour of free ranging groups of tame elephants appear to belong to this latter category. On Smith's[2] standard classification, they can only be classified as 'associative', related to remaining in the company of another individual. However, such signals are commoner by a factor of 20 to 100 amongst elephant calves and their mothers and allomothers when compared to exchanges between adult cows.

We suggest that the function of these signals is mutual monitoring of the state of well being amongst related individuals. The considerable degree of altruistic behaviour displayed in social groups, such as those of elephants is now believed to subserve the function of enhancing the inclusive fitness of the individuals concerned[3]. We explore a mathematical model of exchange of social aid which suggests that animals in social groups may enhance their inclusive fitness further by adjusting the amount of social aid exchanged in relation to the state of well being of the donor as well as the recipient. Our model further suggests that optimal social aid depends on the state of well being in a complex fashion making it difficult for the recipient to deceive the donor so as to extract more aid. We therefore expect that by and large honest communication of the state of well being would be characteristic of the higher social animals.

Such communication would be based on normal physiological changes consequent on a change in well being. Thus animals with a superior degree of well being would take postures conducive to greater activity, would be more receptive to sensory inputs and may also shift the balance of production of various metabolites. This monitoring of the well being has greatly advanced in the human species and may be at the base of the elaborate health care amongst human societies.

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INTERCELLULAR COMMUNICATION IN SOCIAL AMOEBAE: DEVELOPMENTAL AND EVOLUTIONARY EXPLANATIONS

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SOME form of communication between cells – even if only a passive response to mechanical constraints on account of the proximity of other cells – is a prerequisite for multicellular organisation. When one tries to understand intercellular communication, two levels of explanation are possible: one, developmental, invoking immediately preceding or proximate events as causes to be explained; the second, evolutionary, offering an explanation in terms of the contribution of the particular form of communication to organismal fitness. Four features of the life cycle of a particularly simple multicellular organism the social amoeba *Dictyostelium discoideum*, are highlighted with a view to suggest both developmental and evolutionary explanations[1].

(1) *Chemotaxis and relay*: Free-living amoebae feed on bacteria, grow and divide. After the food supply is exhausted the amoebae synthesise and release a chemotactic signal, cyclic AMP, which causes them to aggregate[2,3]. Apart from being a chemoattractant, cyclic AMP is relayed from cell to cell[4,5]. Both chemotaxis and relay enhance aggregate size; they also favour dispersion, because aggregates are motile, and larger slugs move faster than smaller ones[6]. On the basis of the assumption that the relayed molecule is a normal component of the internal response of the cell to environmental stress, it can be conjectured that relaying was selected as a favourable adaptation in a genetically identical group of amoebae subject to starvation[7].

(2) *Periodicity:* The signal molecule, cyclic AMP, is released by *D. discoideum* cells in periodic bursts with a period of a few minutes[8]. On the one hand, periodicity can be a "natural" consequence of a chemical reaction with a positive feedback loop[9]; on the other hand, using reasonable numbers, it can be shown that a periodic signal has a longer range than a steady signal[10]; therefore periodicity too ought to enhance aggregate size.

(3) *Communication within the slug*: Though there is no direct proof of cell-to-cell signalling in the slug, the circumstantial evidence is compelling[11]. A plausible role for such signalling would be as an aid in morphogenesis, that is, in achieving an appropriate spatial segregation of the terminally differentiating cell types.

(4) *Relative proportioning*: The slug eventually differentiates into a fruiting body made up of an erect stalk of dead cells supporting on its top a mound of sporulated amoebae. The ratio of the two cell types is known to be more or less constant. On the assumptions that (i) slime mold aggregates consist of clones, and (ii) the efficiency of spore dispersal increases with the height of the fruiting body, a fixed spore: stalk ratio can be shown to follow.

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TRADEOFFS IN THE EVOLUTION OF FROG CALLS

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ALL biological characteristics are subject to conflicting selection pressures. This is particularly true of those characteristics that are subject to sexual selection. The classic example is the peacock's tail. Others are the calls used by male frogs and toads to attract their mates. The forces which have acted in the evolution of these calls

are varied and the calls that we hear made by these animals are diverse.

Two kinds of factors can be recognized: constraints and forces. Constraints on the kind of a call that a frog might evolve include its phylogeny, the energy required to produce different kinds of calls, the risks incurred from attracting predators. Also important is the morphology of the frog: both the structures used by the males to make the calls and the apparatus with which the females hear the calls. For example, frog size has an important influence both on the frequencies of the sounds that a frog produces and the acuity with which they are heard.

Both passive and active selective forces can be identified. Passive forces include the distances that environments transmit sounds of different frequencies and the interference from other sounds that calls encounter. Active forces include the reactions of conspecific males and females to the calls. Males interact acoustically in a variety of ways to organize their choruses in both space and time. They position themselves, and time their calls so that they minimize the interference from other males while maximizing their chances of securing a mate. Female choice has been studied in test arenas. Females choose louder calls, calls that are most easily located, and the calls of their own rather than other species. In choosing among males of their own species, females have been shown to pick the males controlling the best resources, sometimes using calls to do so. They should also be expected to choose those males who can contribute the best genes to their offspring. The extent to which they do this and the role of calls in choosing is actively being argued.

Sexual selection, both interactions between males and female choice, have undoubtedly been important in the evolution of frog calls but only within the constraints imposed by a variety of other factors.

COMMUNICATION AND SYNCHRONIZATION OF CIRCADIAN RHYTHMS IN INSECTIVOROUS BATS

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CIRCADIAN rhythms, in nature, entrain to the light-dark cycles generated by sunrise/sunset. If the organisms displaying such entrained 24 hr rhythms are brought into constant conditions of light or darkness and invariant temperature of laboratories they 'free-run' (*i.e.* the period deviates from the strict 24 hr periodicity of the geophysical day and of entrained rhythms)[1]. In addition to abiotic factors[2] such as fluctuating cycles of light/darkness, cyclic variations in temperature, the states of the tides in the oceans and even the phases of the moon which are known to be the synchronizers of circadian rhythms, there are also *biotic* factors such as bird songs[3], mother-pup interactions[4], and such other social stimuli which can synchronize circadian rhythms[5]. We have been investigating how the members of a colony of microchiropteran bats inhabiting a true cave under constant darkness, temperature and humidity conditions still time their activity. Such conditions normally, as already explained, release circadian rhythms into freeruns. Results of experiments with trapped bats and flight activity monitoring inside a few such caves indicate that there is clear-cut evidence for social synchronization of the circadian rhythm in the bat *Hipposideros speoris*[6,7]. Bats held captive about 40 m inside a cave in constant darkness still began their nightly activity to coincide with the onset of the foraging activity of the free-flying colony. Obviously the incarcerated bats, were being, socially 'told' of time of local sunset. In further confirmation of the need for conspecific-communication, the results of another experiment inside a cave with a solitary bat with no conspecifics reveal an impressive 'freerun' of its circadian rhythm. (No free flying conspecifics, no social communication and no synchronization.)

Interestingly even the rhythm of an 'alien' bat (*Taphozous nudiventris kachhensis*, an emballonurid species) held captive in the hipposiderid bat cave freeran. Eventhough the social cues emitted by the members of the colony of ca 500 *H. speoris* bats during their outflight soon after sunset and return a little

before sunrise, were available to the captive emballonurid bat, the locomotor (flight) activity of the latter exhibited a freerunning rhythm with a period < 24 hr[8]. Interestingly, the circadian rhythm of a closely related species *H. fulvus* does entrain to social cues of *H. speoris*. However entrainment in the latter case was partial with traits of relative coordination.

In another set of experiments we recorded the flight activity rhythm of *H. speoris* under artificially generated constant light conditions inside the cave. Under constant light conditions of 1 lux two of the three captive bats still entrained to the social cues, and the rhythm of the third bat freerun with a period > 24 hr. The experiment was repeated with an increased light intensity of 10–20 lux, during which interestingly all the captive bats freerun with periods > 24 hr. When the lights were switched off and darkness was restored the freerunning rhythm reentrained to the social cues after a few 'transient cycles'.

We conclude that the social synchronization of circadian rhythms in the bat *H. speoris* is abolished by light of 10–20 lux. Continuous light seems to uncouple the circadian clock from entraining social inputs[9]. Evolutionarily closely related species of bats seem to be able to communicate and synchronize even if only partially and there may be, in a manner of speaking, a 'communication gap' between unrelated species in the context of synchronization of their rhythms.

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Symposium on The Monsoons

AN INTRODUCTION TO THE MONSOONS

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To sailors who travelled across the Arabian Sea to trade with India, the monsoons (derived from the Arabic word mausam, meaning season) were a system of winds that changed direction seasonally. To the inhabitants of India, the monsoons are indelibly associated with rainfall. Although there is a dramatic annual cycle in rainfall, the 'jitter' in this cycle is sufficient to be a source of great national worry and concern, because of the importance of rainfall to the Indian economy. Furthermore the *annual* rainfall varies appreciably from year to year in a rather irregular or chaotic manner, the variance being particularly high in regions of low rain fall. Part of the great difficulty in predicting the monsoons is the vast range of scales that are of interest and the fact that the phenomenon is a complex combination of order (or structure) and chaos. Some progress has been made in recent years in understanding the dynamics of some very simple nonlinear systems exhibiting order and chaos, but much greater understanding of these problems in basic physics and mathematics is necessary before predictability of the monsoons can improve significantly.

THE PHENOMENON

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MONSOONS are a planetary scale phenomenon which have been studied for over a century in our country. Recent studies of satellite imagery have revealed new features of the monsoon cloud band which marks the rain belt over India. One of these is the so called 40 day cycle, in which first a cloud band is generated in the equatorial Indian Ocean; it then moves northward to the Indogangetic plane where it waxes and wanes for a few weeks and disappears. Again a cloud band is generated in the equatorial oceans and the cycle is repeated. This mode has tremendous potential for forecasting the onset of rain and the movement of rain belts few weeks ahead. In addition there is a 15 day oscillation between active monsoon conditions and

dry spells or breaks. The variations within a monsoon season as well as the total monsoon rainfall are determined by relative phases and amplitudes of these modes and deep insight into these intraseasonal and inter-annual variations will be gained in the near future. On the larger time scale of decades we expect that conditions at the surface of land will have an influence and the available studies suggest that deforestation will lead to a decrease in the rainfall on these climatic time scales.

PROSPECTS FOR DYNAMICAL LONG-RANGE PREDICTION OF MONSOONS

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THE day to day changes in weather are mainly due to the growth, propagation and decay of the synoptic scale disturbances which owe their origin to the instabilities of the large scale atmospheric flow. The growth rate for the dominant instabilities and their nonlinear interactions with other scales and the mean flow are such that these synoptic scale disturbances become totally unpredictable within a couple of weeks. This limit of deterministic predictability has been the greatest stumbling block for progress in the dynamical long-range forecasting, and therefore, it is no surprise that in the past most of the attempts for long range forecasting have been either synoptic or statistical in nature. Recent observational and modeling studies have suggested that although the synoptic scales lose their predictability within two weeks, the low frequency planetary scales remain predictable up to a month or beyond and it has also been suggested that there may be additional predictability due to the influence of the slowly varying boundary conditions at the earth's surface. The situation is especially promising in the low latitudes where synoptic scale instabilities are too weak to degrade the predictability of the large scales, and the influence of the changes in the boundary conditions is large enough to be clearly distinguishable from the unpredictable day to day fluctuations.

Changes in the boundary forcings at the earth surface directly influence the location and intensity of the diabatic heat sources which drive the atmospheric circulation. The forcing at the boundary itself is generally not sufficient to produce significant changes in the atmospheric circulation; however, under favorable conditions of large scale convergence and divergence, the boundary effects get transmitted to the interior of the atmosphere and a shallow boundary forcing gets transformed into a three-dimensional heat source which can be quite effective in influencing the dynamical circulation. The effectiveness of a boundary forcing in changing the atmospheric circulation therefore strongly depends upon its ability to produce a deep heat source and the ability of this influence to propagate away from the source. Since both of these factors are determined by the structure of the large scale dynamical circulation itself, the response of a given boundary forcing is very different depending upon its size, geographical location, and structure of the large scale circulation.

The most important boundary forcings are sea surface temperature, soil moisture, surface albedo, snow and ice.

Snow Cover

The possible physical processes which have the potential to influence the atmospheric circulation due to snow anomalies are summarized as follows:

(i) Increase in snow cover increases the albedo, and therefore reduces the incoming solar radiation. If there were not other feedbacks, this would produce colder temperatures, and snow cover anomalies would tend to persist for a longer time.

(ii) Excessive snow anomalies in the mid-latitudes can produce anomalous diabatic heat sources which in turn can produce anomalous stationary wave patterns which can alter storm tracks and their frequency.

(iii) Persistent snow anomalies can change the components of the heat balance of the earth's surface. Even after the snow has melted completely, wet soil can maintain colder surface temperatures for longer periods of time.

(iv) Persistent snow anomalies can produce anomalous meridional temperature gradients and anomalous vertical wind shears which in turn can change the instability characteristics of synoptic scale disturbances.

Sea Surface Temperature

The factors which determine the influence of SST anomalies on the atmospheric circulation are rather complex. The immediate effect of an SST anomaly is to change the sensible heat flux and evaporation. However, this thermal forcing confined close to the ocean's surface is too weak to produce significant changes in the atmospheric circulation. The crucial

factor which determines whether an SST anomaly can produce an atmospheric circulation anomaly is the ability of the SST anomaly to produce a vertically deep heat source in the atmosphere. It is the atmospheric diabatic heat source which produces anomalous atmospheric circulations. Based on several numerical model experiments, it has been suggested that the creation of a strong and deep heat source associated with an SST anomaly depends upon the structure and magnitude of the anomaly, structure and magnitude of the total temperature field, structure of the large scale flow of the atmosphere, the latitude of the anomaly and the most dominant instability mechanisms that produce the energy source to drive the transient circulations in the region. The magnitude of the anomaly is important because it determines the magnitude of change in sensible heat and evaporation; however, due to nonlinearity of the Clausius–Clapeyron equation, the change near the equator is much larger than that at higher latitudes for the same change in the SST. An even more important influence of the structure of the temperature field is its effect on the horizontal convergence of air and water vapor. Small gradients of SST can produce large convergence in the tropics compared to the mid-latitudes and, therefore, can produce large diabatic heating fields. If conditional instability of secumk kind (CISK) is the dominant instability mechanism in the region of anomaly, an enhanced convergence due to horizontal gradients in SST could produce enhanced diabatic heating in the troposphere which would further enhance the moisture convergence in the boundary layer. This feedback mechanism helps to establish a vertically deep heat source in the atmosphere in association with the SST anomaly which is confined to the surface. If a warm SST anomaly occurs in the ascending branches of Hadley and Walker type circulations, it would be more effective in increasing the intensity of these circulations than similar anomalies in the descending branches. Similarly, the location of SST anomaly with respect to the planetary waves in the mid-latitudes may be crucial in determining the response of SST anomalies. If an SST anomaly can produce a deep diabatic heating anomaly, the influence of heating anomaly on the atmospheric circulation would depend upon the structure and magnitude of the heating anomaly and the structure of the large scale flow. In addition to the local influences of the diabatic heating anomaly, there can be significant changes in the circulation away from the anomalies if the intervening medium is suitable for propagation of these influences. Possible mechanisms for the influence of tropical SST anomalies on extratropical circulation are through propagation of Rossby waves on a sphere and changes in the intensity of the Hadley circulation which changes the zonal flow in the midlatitudes which in turn interacts with the quasi-stationary thermal and orographic forcings to produce anomalous atmospheric circulations. The influence of SST anomaly on tropical circulation is mostly determined by the changes in the moisture convergence and precipitation. A warm anomaly could increase the sensible heating, evaporation and moisture convergence, giving rise to enhanced precipitation. If the convergence and evaporation associated with the anomaly is strong enough, it can alter the position and intensity of planetary scale tropical circulations which determine the areas of excessive rain and drought.

Soil Moisture

Since the net diabatic heating of a vertical atmospheric column is maximum over the tropical land masses, it is quite likely that small fractional changes in these asymmetric heat sources could produce considerable changes in the planetary scale circulations of the tropical as well as the extratropical atmosphere. Therefore, in spite of relatively smaller earth surface area being covered by land, soil moisture effects could be as important as SST anomaly effects. The soil moisture effects strongly depend upon season and latitude because during the winter season in high latitudes, solar radiation reaching the ground is not large enough to be important for the surface energy budget. Changes in soil moisture influence evaporation and heating of the land surface. Partitioning of the total radiative energy impinging on the ground into sensible heating and latent heating is determined by the wetness of the ground. If soil is wet, most of the radiative energy goes to evaporate the water and if the soil is dry and there is no vegetation, most of the radiative energy is utilized to heat and ground and the overlying air.

The above discussion of the mechanisms through which boundary forcings influence atmospheric circulation suggests that there is a physical basis for prediction of monthly and seasonal anomalies due to the influence of boundary conditions.

Analysis of past observations has clearly established that the Indian summer monsoon and the global scale "Southern Oscillation" are closely related. Since the Southern Oscillation is also related to the tropical sea surface temperature anomalies (El-Niño), the global scale circulation anomalies are a manifestation of

interactions among monsoons, El-Niño and Southern Oscillation. Because of the long time scale of El-Niño-Southern Oscillation phenomenon, it servers as a useful predictor for a highly periodic phenomena like the monsoons.

Other Lectures

EXCURSIONS INTO MULTIPHASE REACTIONS

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MULTIPHASE reactions are ubiquitous and crucial in chemical industry and encompass a wide variety of systems. A rational analysis of reactors where such reactions are conducted requires an intimate knowledge of chemical kinetics, thermodynamics, mass transfer and fluid mechanics.

The theory of mass transfer with chemical reaction is immensely helpful in studying complex reaction systems and even allows a study of kinetics of exceedingly fast reactions and prediction of selectivity. It is possible to imaginatively exploit kinetic versus thermodynamic factors to achieve selectivity in a variety of two and three phase reaction systems.

In many cases of practical importance it may be advantageous to convert homogeneous reaction systems into two-phase systems to allow the use of cheaper reactants, milder operating conditions, ease of removal of the desired product, higher selectivity with respect to the desired product, etc. Even in the case of solid catalysed vapour phase reactions we may benefit by using an additional liquid phase. In some catalytic hydrogenations the use of second liquid phase can lead to a drastic change in the selectivity. Some gas-liquid reactions benefit by changeover to liquid-liquid mode due to much higher interfacial area in the latter case.

A number of new strategies have been suggested to further intensity rates in multiphase reactions and these include phase transfer catalysis, micellar catalysis, microemulsions, use of hydrotropic substances, change-over to supercritical conditions, use of a second liquid phase, use of fine catalyst or inert particles etc. In particular the role of catalyst or reactant particles or liquid droplets smaller than diffusion film thickness can be crucial. It is important to recognise differences between occurrences in the diffusion film versus bulk liquid phase. Thus it can be shown as to how HClO can be stripped when chlorine diluted with an inert gas is absorbed in strong aqueous caustic soda solutions even though a huge excess of hydroxyl ions may exist.

Multiphase reaction systems are very helpful in the recovery of a variety of toxic and refractory chemicals from dilute aqueous waste streams. Multiphase reaction systems are now acquiring importance in biochemical and electrochemical reaction systems where introduction of an additional liquid phase bestows some important benefits.

Multiphase reactions are relevant in high polymer industry and complex situations arise due to complications associated with fluid mechanics.

Modelling of industrial reactors is immensely helpful and often allows higher throughout to be realised from existing assets. In some cases selectivity can be improved. It is necessary to examine aspects of stability of reactors.

ELECTRON DENSITY IN CHEMISTRY*

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OVER the past few years, the density functional (DF) theory[1] has evolved as a conceptually, and, to some extent, practically useful method for studying the electronic structure of many-electron systems. The charm of the electron density is twofold: (a) It is a 3-dimensional entity, rather than the 3N-dimensional wavefunction and (b) can be measured experimentally[2]. The density-based approach has had a long history, beginning with the celebrated Thomas-Fermi theory[3], followed by several refinements such as the Thomas-Fermi-Dirac and Thomas-Fermi-Dirac-Weizsäcker models. However, the rigorous justification for the use of electron density as a basic variable was provided by the pioneering work[4] by Hohenberg and Kohn (HK) in 1964. The main theorem in their work may be summarized as follows: For the (non-degenerate) ground state of an arbitrary collection of electrons moving under an external potential $V(\vec{r})$ and their mutual repulsions, the electron density, $\rho(\vec{r})$ is a unique functional of $V(\vec{r})$ *and conversely*.

Here,

$$\rho(\vec{r}_1) = N \int |\psi(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_n)|^2 \, d\vec{r}_2 \, d\vec{r}_3 \ldots d\vec{r}_n,$$

ψ being the N-electron wave function. Thus, one may write the electronic energy, E, a functional of $\rho(\vec{r})$ as a sum of two ingredients:

$$E[\rho] = F[\rho] + \int V(\vec{r})\rho(\vec{r})\, d\vec{r} \qquad (1)$$

where, $F[\rho]$ is a universal functional[4]. The variational principle holds for V-representable densities (*i.e.* the densities which are ground state solutions corresponding to *some* external potentials, $V(\vec{r})$):

$$E[\rho] \geq E[\rho_{g.s}] \qquad (2)$$

This means that *any* V-representable density, ρ, other than the exact ground state density would correspond to a higher electronic energy than $E_{g.s}$. The V-representability problem has been circumvented[5] by an ingeneous construction of a new functional

$$Q[\rho] = \underset{\psi \to \rho}{\text{Min}} \langle \psi | \hat{T} + \hat{U} | \psi \rangle \qquad (3)$$

where, the search is carried out over a set of antisymmetric wavefunctions leading to the density, $\rho(\vec{r})$; $\hat{T}$ and $\hat{U}$ are the kinetic energy and electron-repulsion operators respectively. The functional $Q[\rho]$ conforms to the variational principle and coincides with $F[\rho]$ for V-representable densitites.

The chief problem associated with the HK formalism is that though $F[\rho]$ is a *universal* functional, its exact form is, as yet, unknown. A practical scheme for solutions of atomic and molecular problems has been proposed by Kohn and Sham in the form of self-consistent equations[6]:

$$[-\tfrac{1}{2}\nabla^2 + V_{\text{eff}}(\vec{r})]\phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) \qquad (4)$$

where, $V_{\text{eff}}(\vec{r})$ is the sum of the electrostatic and exchange-correlation potentials,

$$V_{\text{eff}}(\vec{r}) = \phi(\vec{r}) + V_{xc}(\vec{r}) \qquad (5)$$

The electron density is given by

$$\rho(\vec{r}) = \sum_{i=1}^{\text{occupied}} |\phi_i(\vec{r})|^2 \qquad (6)$$

Several approximations[7] for the exchange-correlation functional have been proposed and employed in actual calculations, the most popular being the local spin-density approximation and its variations[8,9]. Henderson[10] has recently formulated the density functional theory in the momentum space and a first-ever DF model[11] in momentum space has been worked out.

Apart from providing a practical scheme for working out atomic and molecular properties, DF theory has been useful for analysing of chemical concepts, some of which are listed below:

1. Electronegativity has been identified as the Lagrange multiplier in the Euler-Lagrange equations[12]. Electronegativities of elements have been worked out[13] from atomic X_α theory.
2. 'Hardness' has been identified[14] as $(\partial\mu/\partial N)$.
3. Providing an understanding of homogeneity characteristics and scaling of functionals, and deriving rigorous bounds to them[15].
4. Establishing approximate connections[16] between the coordinate and momentum space properties.

It is hoped that the density-based approaches would enable us to obtain better numbers. More importantly, they will lead us to a better understanding of several basic concepts in chemistry.

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BIOMIMETIC MODEL REACTIONS IN PHOTOSYNTHESIS

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BIOMIMETISM implies duplication of functions performed by molecular entities in biological systems either by modifying or isolating certain salient features pertinent to the real systems. Laboratory simulation of natural photosynthetic process is one of the most fascinating problems since it provides an important and promising pathway for the production of O_2 and fixation of CO_2 using solar irradiance under optimal conditions. Successful accomplishment of biomimetic devices, to a large measure, depends upon the understanding of the structure and organization of the molecular entities present in the real systems and their *in vivo* mechanistic aspects.

The basic feature of natural photosynthesis is that it represents a complex set of light-induced electron transfer processes for the conversion and storage of solar energy. The photosynthetic pigments chlorophylls (Chl) occur *in vivo* non-covalently bound to protein forming two functionally and spectrally distinct classes; the photochemical reaction-centre (RC) and light harvesting system (antenna). The latter acts as a photon concentrator controlling the photon flux and channel them to one of the RCs through efficient energy-transfer process. The primary photochemistry in RC is the ultrafast charge-separation resulting from the singlet excited state of the donor, Chl and the primary acceptor. The secondary acceptors are strategically located in the RC to accomplish the spatial separation of charges so as to avoid the wasteful charge-recombination reactions. It is essential that the biomimetic model compounds should have these built-in features to duplicate the fast energy transfer and light-induced electron transfer acts exhibited by the natural photosynthetic systems.

Synthetic reaction-centres to mimic charge-separation process involve cell-free pigments, Chl and its altered products, pyrochlorophillide, pheophorbide and pheophytin, and their structurally analogous compounds, porphyrins. The dimeric, trimeric and tetrameric pigments have been extensively studied as models for the light induced electron transfer process. Investigations on an interesting tetrameric compound, comprising of a pyrochlorophyll *a* dimer covalently attached to two pyropheophytin *a*, reveal a close similarity to the RC complex in the display of rapid photo-induced electron transfer accompanied by slower charge-recombination reaction. In this system, the dimeric pyrochlorophyll *a* was shown to function as a donor and the pheophytin *a* as an acceptor. Model studies on covalently and non-covalently linked bis-porphyrins and porphyrins endowed with the acceptor entities *viz* quinones, nitroaromatics, carotenes and others have considerably improved our understanding of the factors contributing to the ultra-fast charge-separation process. It is estimated that an inter-chromophore separation of 7–9 Å favour the light-induced charge separation process in these model compounds. The roles played by the orientation of the acceptor entities and the medium effects are, however, remain unclear. In most of these systems, the free-energy change for the singlet excited state electron transfer from the pigment to the acceptor is largely exergomic.

The bimimetic model studies in the last three years have focussed attention on the importance of distal and orientational factors on the photo-induced electron transfer process. These studies offer more flexibility in terms of structural design than the real systems and pave way for the search of fuel producing systems. Research in this area has improvised many known techniques and herald newer methods such as Reaction yield detection by magnetic resonance (RYDMR), Optical detection by magnetic resonance (ODMR) and others, to probe into the characterisation of transient species having very short life times. *In vivo* and *in vitro* experimentation employing bimimetic models offer a good scope for studying multitudes of reactions involving many electron transfers *viz* reduction of sulphite and nitrate respectively to sulphide and ammonia, water- splitting to H_2 and O_2 under ambient conditions, and others.

STRUCTURE, CONFORMATION AND CHARGE DENSITY STUDIES BY X-RAY DIFFRACTION

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EVERSINCE the discovery in 1912, x-ray diffraction techniques have paved the way for many exciting investigations in several branches of science, have solved many intricate problems and have contributed immensely to the development of structural chemistry. With the advent of automatic diffractometers and high speed computers over the last three decades, it has become possible to collect and process large amounts of very accurate x-ray data. Two major contributions have come out of this; one is the structure solution of very large molecules like proteins, enzymes and viruses and the other is the study of charge density distributions.

X-ray scattering is a phenomenon involving essentially the electron cloud around an atom in a given material; the charge density is the main information which is readily obtained. If the material is a single crystal, then the molecules are governed by certain rules of packing and so is the scattering from the atoms in the molecule. The determination of the structure involves the recognition of the arrangement of atoms in the molecule followed by the arrangement of molecules in the unit cell, this follows from an analysis of the diffraction of x-rays from the single crystal. When once the spatial arrangement of atoms is recognized, the configurations corresponding to the potential energy minima are known as conformations. Eventhough, x-ray diffraction studies do not yield the energies involved directly, the arrangement of atoms as deduced in a molecular crystal is not far from the minimum energy conformer. Clearly, when an atom becomes a part of the molecule, the otherwise spherical electron cloud gets deformed due to the interaction with the neighbouring atoms. These deformations, though small, are significant from the point of view of charge density distribution over the entire molecule or the crystal. Infact, it is these deformations which endow the molecule with topological properties like net charges, dipole and higher moments and electric field gradients.

The methods of structure solution are now very well established. The emphasis is therefore mainly on the possible chemical reactivity and its role towards better understanding of structure-activity relationships. The available data[1] itself can be utilized to analyse the chemical behaviour of a given moiety, molecule or a ligand[2,3]. Conformational flexibility of an otherwise rigid molecule due to substitution, inter and intra-molecular effects gives a handle to study the energetics of the system. Such molecular mechanics studies in terms of structures determined by x-ray diffraction yield several interesting results[4].

The deviation from spherical symmetry in atoms when they become a part of a molecule can be studied with very accurate low temperature x-ray data[5] by computing the deformation density

$$\rho_{\text{deformation}} = \rho_{\text{expt}} - \sum_{\text{all atoms}} \rho_{\substack{\text{spherical,}\\ \text{isolated atoms}}} \qquad (1)$$

Expressing (1), in terms of x-ray diffraction structure factors

$$\rho_{\text{deformation}} = \frac{1}{V}\sum (F_0 - F_c) \exp 2\pi i\, S.R. \qquad (2)$$

where F_0 = Experimental structure factor
F_c = Promolecule (atoms before molecule formation) structure factor

F_c is obtained either from neutron data or from high order x-ray data. Such charge density distribution (deformation) maps show features of bonding, lone-pair densities and intermolecular interactions. Mathematical methods for the analysis of charge densities from such data have been developed[5,6] to derive one-electron properties. Parallel developments in theoretical methods have also paved the way for an interpretive analysis of such deformation maps[7].

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DEVELOPMENT OF NUCLEAR ENERGY IN INDIA PARTICULARLY SUCCESSFUL THIS YEAR*

THE development of peaceful uses of atomic energy in India has been particularly successful this year. The performance of our power reactors has improved considerably. The first indigenously built 235 MWe heavy water reactor of the Madras Station started commercial operation in January 1984 and has attained an availability factor of over 80 per cent during the year and the second reactor of the Rajasthan Station over 86 per cent. The reactors at the Tarapur Station attained an availability factor of nearly 93 per cent (if one excludes the refuelling outage time). All the necessary support needed for our future nuclear power programme is now within the competence of Indian industries. The heavy water plants at Tuticorin and Baroda have got over their prolonged teething troubles and are now working satisfactorily. The heavy water plant at Kota has also begun production. With these successes, a programme for installing 10,000 MWe of nuclear power by the end of this century has been drawn up. This represents about 10 per cent of the total generating capacity in India at that time. The successful operation of the indigenously built reprocessing plants has enabled us to move towards the second phase of the nuclear power programme based on fast breeder reactors. The plutonium-uranium carbide fuel for the Fast Breeder Test Rector is presently under fabrication and the reactor is expected to become critical by the end of this year. A small uranium-233 solution reactor, called PURNIMA-II, reached critically in May this year and studies of the thorium cycle are in progress. The 100 MW (thermal) heavy water research reactor, DHRUVA, meant for isotope production and basic and engineering research, is expected to become critical in October this year.

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While there is no doubt that atomic energy is today being used for power generation in the developed countries in a big way, and to a lesser extent in some developing countries like India, the benefits of atomic energy to most developing countries have been disappointingly small. It is not that they do not require energy. It is that the anti-nuclear propaganda, so often aired in the developed countries, who are themselves using nuclear energy to a great extent, has created misconceptions in the minds of planners in developing countries. The Director General has also said that anti-nuclear propaganda is perhaps being propounded mainly for political reasons. I feel very strongly that the time has now come to remedy this situation. India's experience has demonstrated that atomic energy is not only safe, but is also competitive with other alternative sources of energy.

As the Director General pointed out in his statement, over 300 nuclear power plants are now operating, supplying 12 per cent of the world's electrical energy and another 200 are under construction. After more than 3100 reactor-years of operation, the overall nuclear safety record continued to be positive. Although there were some incidents caused by human failures or technical problems, no accidents of any significant consequence occured at any of the power reactors. The nuclear industry's contribution to total world wide radiation exposure continues to be minimal and less than one per cent that from natural sources.

If it is not the safety record of the nuclear industry that has created this aura of impending gloom, is it the fear of proliferation? Proliferation of nuclear weapons is indeed terrible and poses a threat to humanity's very existence, but a nuclear power station in a developing country does not necessarily lead to nuclear weapons. The nuclear weapons that today threaten mankind with extinction continue to be made by the dedicated weapons programmes of nuclear weapon states. The record of nuclear energy programmes outside the nuclear weapons state does not justify the exaggerated fears and propaganda, to the extent of even imposing restrictions on the free exchange of scientific ideas. It seems rediculous to place restrictions on transfer of scientific information. After years of progress in advancing knowledge in the world, it is surprising that we cannot ask for information from one another. History has proved time and again that if information is denied, it has invariably been generated by that country itself.

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* Extract of Lecture delivered by Dr. Raja Ramanna, Chairman, Atomic Energy Commission, Leader of the Indian delegation to the 28th General Conference of the International Atomic Energy Agency at Vienna on September 24, 1984.