

Electrons in Molecules

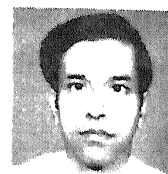
B M Deb

The electron density distribution in a molecule determines its stability, geometry and reactivity, in short its chemistry.

“What are electrons doing in molecules?” This is a deceptively simple question that scientists have been trying to answer for more than eighty years. With the advent of quantum mechanics in 1926, it became clear that we must understand the dynamics of electronic motion in atoms, molecules and solids in order to explain and predict physical, chemical and biological phenomena.

Since the electrons are doing many ‘things’ in molecules, let us restrict ourselves to a few essential concepts. The interlinked, conceptual framework of chemistry is: *bonding (or binding), structure and properties (including reactivity) – both static (independent of time) and dynamic (dependent on time), non-relativistic as well as relativistic*. In this article, we would try to understand chemical binding, molecular geometry and molecular reactivity in a simple manner, from a static, non-relativistic viewpoint (note – even the H atom and H₂ molecule are not as simple as they appear to be).

First, consider the problem of *chemical binding*. *How is a chemical bond formed?* Consider the simplest molecule, H₂⁺, where two protons are held together by one electron. Using atomic units (a.u.), we ask: if the protons are separated by unit distance, what fraction of the electronic charge must be placed at the mid-point between them so that we have a stable system, i.e., there is no net force on any proton? Interestingly, the answer is a small fraction, only one-fourth. We thus see that *electron–nuclear attractive forces are primarily responsible for chemical binding*. Furthermore, since the energy of H₂⁺ in the ground state must be lower than that of an H atom in the ground state, the negative (attractive) forces in the H⁺-H interaction must play the dominant role.



B M Deb is currently Professor of Theoretical Chemistry at Panjab University, Chandigarh and Honorary Professor at the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore. He did his D.Phil. in 1969 at the Mathematical Institute, Oxford University, U.K. under the supervision of late Professor C A Coulson. His research works have dealt with various aspects of electron density in chemistry, in particular, forces in molecules, density functional theory and quantum fluid dynamics. He is also deeply interested in chemical and science education as well as the interface between chemistry and fine arts.

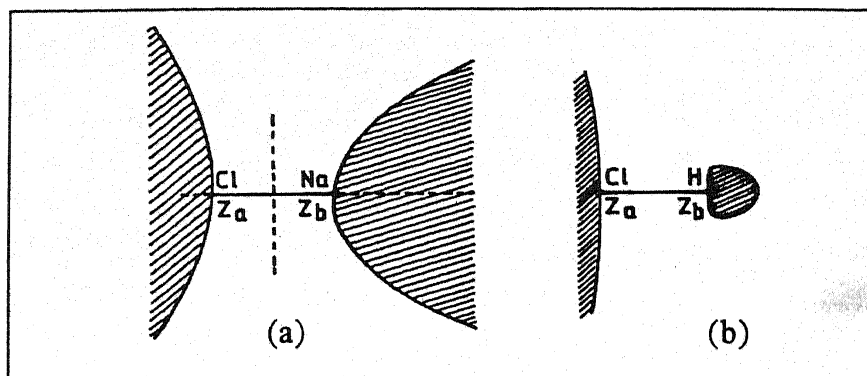
By invoking certain assumptions, based on the fact that the nuclei in a molecule move rather sluggishly, compared to the electrons, the above simple classical description can be placed on a quantum-mechanical footing. To do this, we regard the electron not as a static point charge but as an entity which is described by a quantum-mechanical electron density $\rho(\vec{r})$ which is a continuous function and, on integration over the *entire* three-dimensional space, gives the total number of electrons in a system. Therefore, an adequate extent of electron density should be 'smeared' *between* the two nuclei as a 'cement' for binding the nuclei. It is also clear that *even a slight concentration of electron density on the internuclear axis between the two nuclei goes a long way in binding them.*

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For the ground state of a molecule, the electron density tends to accumulate in the vicinity of a nucleus (because this is the region of the lowest potential energy), falling off exponentially at larger distances. Clearly, for an A_2 molecule, going along the internuclear axis from one nucleus to another, $\rho(\vec{r})$ would have a *minimum* at the bond mid-point. But if we travel along a perpendicular bisector of the A-A bond, $\rho(\vec{r})$ would have a *maximum* at the bond mid-point. Thus, the mid-point in an A_2 molecule is a *saddle-point* in $\rho(\vec{r})$. For an AB molecule, the saddle-point on the internuclear axis would be away from the bond mid-point.

If the electron density is placed in the region *between* the two nuclei, it tends to bind the nuclei, i.e. it causes attraction between them. But, if electron density is placed *behind* a nucleus on the internuclear axis, it tends to separate the nuclei since it attracts the nearer nucleus more strongly than the other nucleus, i.e., it causes repulsion between them. Thus, depending on the nature and extent of the quantum-mechanical distribution of electron density in a diatomic molecule, electron-nuclear attractive forces can cause either attraction or repulsion (apart from nuclear-nuclear repulsion) between the nuclei. The

Figure 1. Contours of the boundary surfaces (solid curves) separating the binding from antibinding (hatched) regions in (a) NaCl and (b) HCl. Z_a and Z_b are nuclear charges.



molecule becomes stable when there is no net force on any nucleus, i.e., the sum of all attractive and repulsive forces vanishes at the equilibrium configuration.

The above argument implies that we can divide the entire three dimensional space around the two nuclei into *binding* (where electron-nuclear attraction due to $\rho(\vec{r})$ binds the nuclei) and *antibinding* (where electron-nuclear attraction due to $\rho(\vec{r})$ separates the nuclei) regions. The boundary surfaces separating the binding from the antibinding regions are defined by the relation

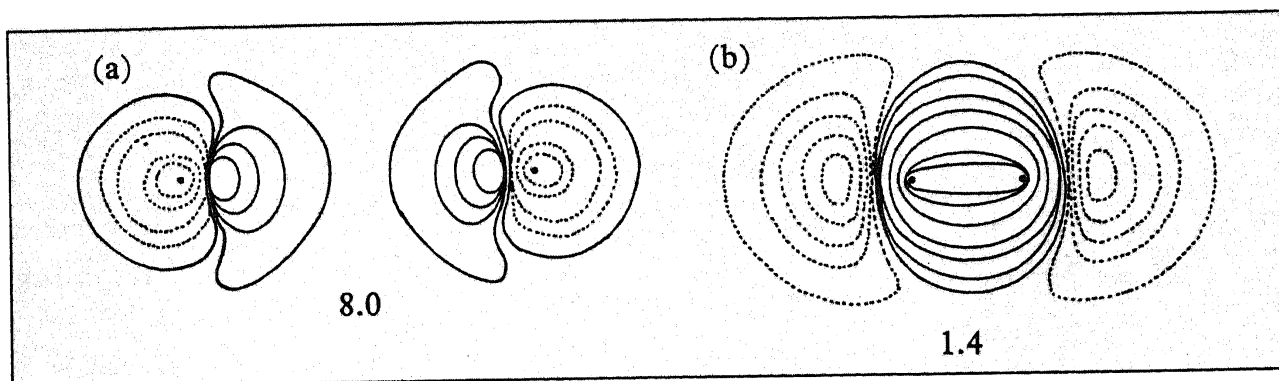
$$f_{A_z} = f_{B_z} \quad (1)$$

where

$$f_{A_z} = -Z_A \int \rho(\vec{r}) \frac{z_A}{r_A^3} dV, \quad (2)$$

z is taken along the internuclear axis, f_{A_z} is the z -component of the electron-nuclear attractive force on the nucleus A of charge Z_A , z_A and r_A are the corresponding coordinates measured from A . Any electron density placed on the boundary surfaces (Figure 1) causes neither attraction nor repulsion between the nuclei. These arguments can be extended to polyatomic molecules.

In the light of the above reasoning, let us now try to understand the bond formation in the H_2 molecule by letting two H atoms in the ground state approach each other from an infinite



distance until they begin to interact. If we write ,

$$\Delta\rho(\vec{r}, R) = \rho_{\text{mol}}(\vec{r}, R) - \rho_{\text{atoms}}(\vec{r}, R), \quad (3)$$

where R is the internuclear distance, ρ_{mol} is the electron density of the *entire* system at R and ρ_{atoms} is the sum of the two separated atomic densities at R , then $\Delta\rho$ is a continuous function which clearly reveals the nature of electronic charge reorganization occurring as a result of the interaction. In particular, those regions of space where $\Delta\rho$ is positive have an accumulation of electron density whereas regions of space with negative $\Delta\rho$ suffer a depletion in electron density (note that $\Delta\rho$, integrated over the whole three-dimensional space, would give zero). *Figure 2a* shows that, at $R = 8.0$ a.u., the individual atomic densities get polarized *even though they do not yet overlap*, and two atomic dipoles pointing to each other are formed. For each dipole, the centre of negative charge lies towards the other nucleus so that each nucleus is dragged towards the other by its own electron density. This is the origin of the long-range dipole-dipole attraction force which is proportional to $1/R^7$. At smaller R , the two atomic densities overlap. However, the mere overlap of atomic densities (or, of atomic orbitals) does not lead to a chemical bond. *A necessary but not sufficient condition for the formation of a chemical bond is that $\Delta\rho$ should be positive in the binding region.* For H_2 , this condition is fulfilled at $R_{\text{eq}} = 1.4$ a.u. (*Figure 2b*); note also that $\Delta\rho$ is positive in parts of the antibinding regions behind the two nuclei. *Figure 3* shows that for He...He interaction at $R = 2.5$ a.u., $\Delta\rho$ is positive in some parts of the

Figure 2. Contours of the difference density $\Delta\rho(\vec{r}, R)$ for the H_2 system at (a) $R = 8.0$ a.u. and (b) $R_{\text{eq}} = 1.4$ a.u. The solid and dotted curves denote positive and negative $\Delta\rho$ respectively. The dots indicate nuclear positions.

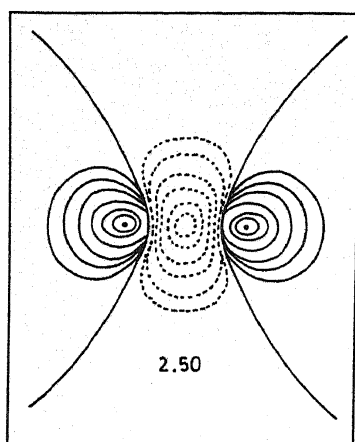


Figure 3. Contours of the difference density $\Delta\rho(\vec{r}, R)$ at $R = 2.50$ a.u. for the He_2 system. The solid and dotted curves denote positive and negative $\Delta\rho$ respectively. The dots indicate nuclear positions.

binding region; however, He_2 is unstable. Thus, *the nature and extent of the distribution of positive $\Delta\rho$ in the binding region decides the formation of a chemical bond.*

The above arguments can be extended to polyatomic molecules. But, now *both the sizes and shapes of molecules* enter into consideration. It is a fundamental principle in quantum chemistry that *a system is stable when its total energy is a minimum with respect to all the parameters involved.* If we envisage a polyatomic molecule to be formed from its constituent atoms and ions then, along with bond formation, molecular geometry (bond lengths, bond angles and conformational angles) is decided as the minimum-energy configuration. As mentioned before, at this configuration, there is no net force on any nucleus in the molecule. Since the electron-nuclear attractive forces are primarily responsible for lowering the total energy (see previous arguments on bond formation), obviously they must also be the deciding factor in governing molecular shapes (bond angles and conformational angles). Therefore, we now try to understand *how electron-nuclear attractive forces decide molecular shapes.* Here too the electron density plays a fundamental role.

Consider *Figure 4a* in which the nuclei in an AB_2 molecule are in a non-equilibrium triangular configuration. If the major part of the electron density is inside the triangle, it would exert transverse electron-nuclear forces on the B nuclei in the inward direction, causing the molecule to be bent. But, if the major part of the electron density is outside the triangle (*Figure 4b*), the transverse electron-nuclear forces on the B nuclei would be in the outward direction, causing the molecule to be linear. Within

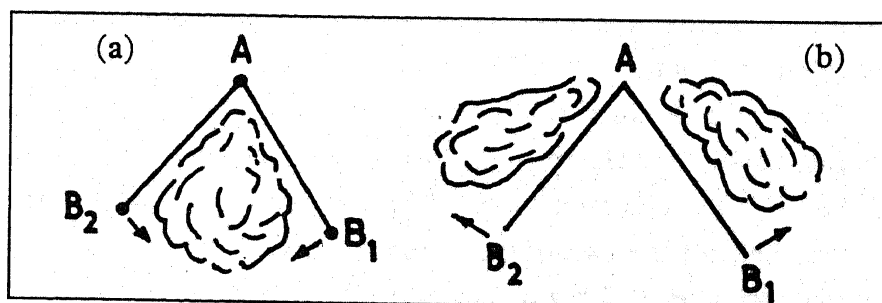


Figure 4. Electron clouds and transverse electron-nuclear attractive forces leading to (a) bent and (b) linear AB_2 molecules.

the molecular-orbital (MO) approximation, the net electron density in a molecule is a sum of occupied MO densities (the square of a real MO, multiplied by the number of electrons occupying the MO, gives the MO density). If we wish to obtain the resultant force exerted on a nucleus by all the MO densities, we must compute all the individual forces (see (2)). However, for qualitative explanations and predictions of the shapes of a large number of molecules, we may avoid such computations by focussing attention on only one MO, *viz.*, the HOMO (highest occupied MO).

Let us make the following assumption and see how far it takes us: "The gross equilibrium molecular shapes are decided primarily by the electron–nuclear attractive forces generated by the electron density in the HOMO. If the HOMO is insensitive to shapes, then the next lower MO is to be examined and so on" (HOMO Postulate).

As an application, consider AH_2 molecules with up to 8 valence electrons. Their schematic valence MOs (Figure 5), with energy order, may be obtained without computation, by using s and p atomic orbitals (AOs) along with symmetry considerations. The MO energy order is: $1a_1$ (bonding) < $1b_2$ (bonding) < $2a_1$ (essentially non-bonding or feebly bonding) < $1b_1$ (non-bonding). From Figure 5, we conclude that $1a_1$ and $2a_1$ densities exert transverse forces on the two protons in the inward direction, $1b_2$ density exerts transverse forces in the outward direction while $1b_1$ density does not exert any transverse force on the protons, thus being insensitive to molecular shape.

Therefore, using the HOMO postulate, AH_2 molecules containing 1, 2, 5–8 valence electrons should be bent in their ground states whereas those with 3 or 4 valence electrons should be linear. A 4-valence-electron linear AH_2 molecule (e.g., BeH_2) would be bent in the singly excited state in which the HOMO is $2a_1$. A 5-valence-electron bent molecule (e.g., BH_2) would become linear if the electron in the $2a_1$ HOMO is excited to $1b_1$ MO.

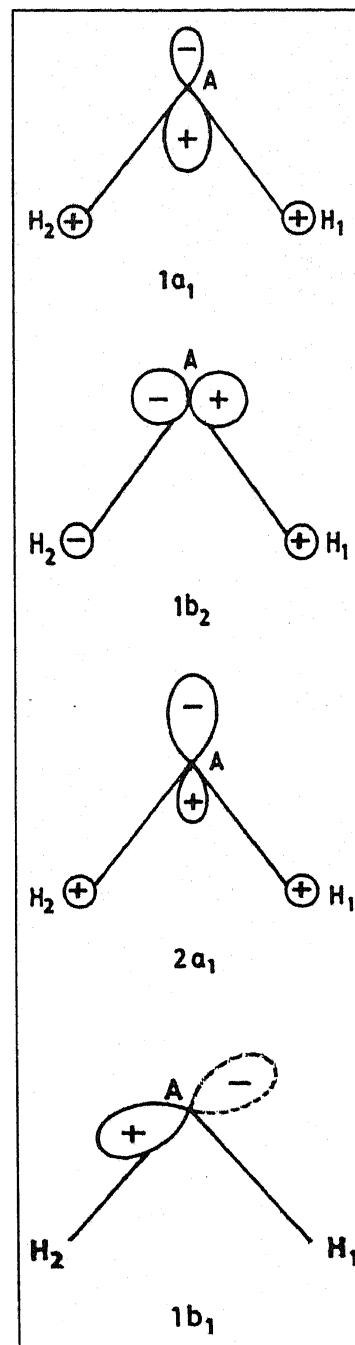


Figure 5. Schematic MOs for bent AH_2 molecules, using s and p valence AOs. From these, schematic MOs for linear molecules can be readily obtained. The $1b_1$ MO is a pn AO on A, perpendicular to the molecular plane.

If the idealized ground state of a non-linear polyatomic molecule is degenerate (orbital and/or spin degeneracy), then Jahn–Teller distortion to a lower molecular symmetry is likely to take place.

These predictions according to the HOMO postulate are correct. The case of the ground state (triplet) of CH_2 molecule is instructive. Since the HOMO is $2a_1$, the ground singlet (all MOs doubly occupied) is bent, with an observed bond angle of 104° . When an electron in the $2a_1$ MO is excited to the insensitive $1b_1$ MO, the bond angle should increase (the observed angle is 140°). The triplet ground state has the same orbital occupancy as the excited singlet. Hence, the triplet should have a bond angle close to 140° ; the actual value is 136° .

The above arguments on molecular shapes in ground and excited states, in terms of electron–nuclear attractive forces, may be extended to a number of molecular classes, embracing many molecules. They may also be employed to explain the shape of a *fragment in a molecule* (e.g., CH_2 in CH_4 , SF_2 in SF_4 , XeF_2 in XeF_4 , etc.) as well as explain the variations in bond lengths, bond angles, conformational angles, barriers to internal rotation/inversion, stretching/bending force constants, etc. However, when a molecule is quite large, with many occupied MOs, it is not advisable to bypass the actual computation of forces.

As another application of the above approach, consider the Jahn–Teller distortion in the VC1_4 molecule. *If the idealized ground state of a non-linear polyatomic molecule is degenerate (orbital and/or spin degeneracy), then Jahn–Teller distortion to a lower molecular symmetry is likely to take place.* VC1_4^+ molecule is a regular tetrahedron with a non-degenerate ground state. In VC1_4 , the extra electron may go into either (or a linear combination) of two degenerate MOs which are essentially d_{z^2} and $d_{x^2-y^2}$ AOs of the vanadium atom. As a result, the molecule should be distorted to a symmetry lower than tetrahedral (cubic). *Figure 6a* shows that if the electron goes into the d_{z^2} orbital, the transverse electron–nuclear forces would elongate the tetrahedron along the z-direction. *Figure 6b* shows that if the electron goes into the $d_{x^2-y^2}$ orbital, the transverse electron–nuclear forces would flatten the molecule in the z-direction. Since the two distortions are of opposite signs, the

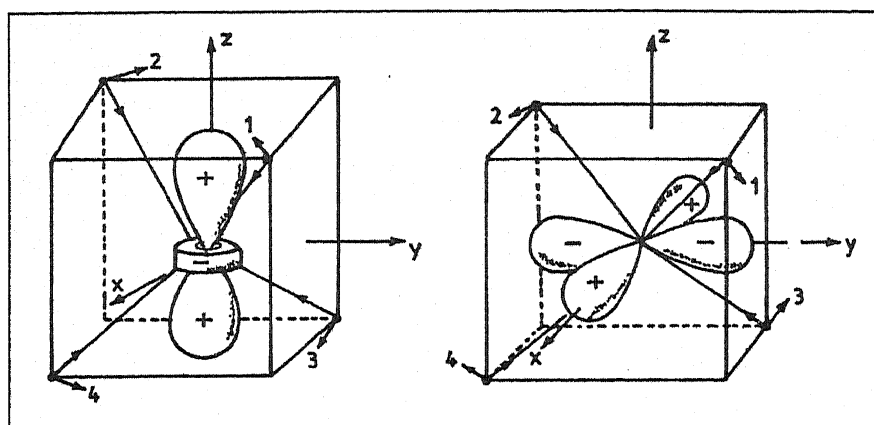


Figure 6. The Jahn–Teller distortion in VCl_4 , using vanadium (a) d_{z^2} and (b) $d_{x^2-y^2}$ AO. The arrows on ligand atoms indicate their movement due to both longitudinal (along V–Cl bonds) and transverse (perpendicular to V–Cl bonds) electron–nuclear attractive forces. In (a) transverse forces elongate the tetrahedron while in (b) they flatten the tetrahedron.

electron would tend to avoid a linear combination of the two AOs because then the stabilization energy due to distortion would be less. The actual computation of stabilization energies does not show a preference for either the flattened or elongated tetrahedron. Therefore, we conclude that the ground state of VCl_4 is a fifty-fifty mixture of flattened and elongated tetrahedra; experimental results indicate an approximately sixty-forty mixture.

So far, we have seen that the interconnected phenomena of chemical binding and molecular geometry can be understood from a common, unifying standpoint of electron–nuclear attractive forces. The question arises: *Can we approach molecular reactivity from the same standpoint?* Since chemical reactions involve essentially the breaking and making of bonds, and molecular geometry plays a subtle role in nudging the reactant molecules along specific pathways, the answer is *yes*.

Consider the formation of ethane (C_2H_6) molecule from two methyl (CH_3) radicals in their ground states, approaching each other from a large distance. At a sufficiently short distance, when the interaction begins, if the CH_3 radicals remain in their initial, almost planar shapes, the calculated net force on a carbon nucleus is always directed *away* from the other carbon nucleus. Therefore, the reaction is not favoured. However, when the interaction begins, if the two CH_3 radicals relax their shapes to become more and more pyramidal (eventually, the HCH angle

Box 1

The time-independent Schrödinger equation based on which the electronic structures and properties of atoms, molecules and solids have been studied for the last seventy years, is given by

$$H\Psi_0 = E\Psi_0$$

where H is the Hamiltonian operator, E is the total energy of the system and Ψ_0 is the wavefunction which is assumed to contain *all* information about the stationary states of the system. The Hamiltonian contains many terms.

H = Nuclear kinetic energy + electronic kinetic energy + electron nuclear attraction + electron–electron repulsion + nucleus–nucleus repulsion + electron “orbit–orbit” interaction + electron spin–“orbit” interaction + electron spin–spin coupling + electron spin–nuclear spin coupling + electron “orbit”–nuclear spin coupling + nuclear spin–spin coupling + external electric and magnetic field-dependent terms.

To the total energy E thus obtained, one may add relativistic corrections.

The time-dependent Schrödinger equation is (\hbar is Planck's constant)

$$H\Psi = i\hbar (\partial\Psi/\partial t), \quad i^2 = -1, \quad \hbar = h/2\pi$$

For a stationary state,

$$\Psi = \Psi_0 \exp [-iEt/\hbar].$$

in a CH_3 would approach the tetrahedral value) as they approach each other, then the net calculated force on any carbon nucleus is directed *towards* the other carbon nucleus. Therefore, the two radicals would attract each other, leading to the formation of the C–C bond such that the CH_3 fragments in C_2H_6 have the right geometry. This simple example illustrates that chemical binding, molecular geometry and molecular reactivity are subtly interconnected and any separation between them would be artificial. Furthermore, all these electronic phenomena should be understood from a unifying conceptual viewpoint.

Apart from forces, certain molecular reactions may also be understood by using a closely related classical concept, viz.

the molecular electrostatic potential (ESP), $U(\vec{r})$, which is experienced by a unit positive charge as it is brought from an infinite distance to the molecule (note that force is the negative gradient of the potential energy function). Within the same conceptual framework as the forces, $U(\vec{r})$ is given in terms of the quantum-mechanical electron density $\rho(\vec{r})$ as

$$U(\vec{r}) = \sum_A Z_A / |\vec{R}_A - \vec{r}| - \int (\rho(\vec{r}') / |\vec{r}' - \vec{r}|) dV' \quad (4)$$

where \vec{R}_A denotes the position of nucleus A and the summation extends over all nuclei in the molecule. The first term on the right-hand side of (4) is due to nuclear repulsion while the second term is due to electronic attraction. The calculated molecular ESP map shows the presence of a number of minima of varying depths (Figure 7) where an approaching positive charge or an electrophile tends to attach itself. The ESP has been extensively employed to explain the mechanisms of electrophilic reactions. It has been hailed as "the most significant discovery in quantum biochemistry in the last thirty years".

Suggested Reading

- ◆ B M Deb. *Rev. Mod. Phys.* Vol. 45, 22, 1973.
- ◆ B M Deb. *J. Am. Chem. Soc.* Vol. 96, 2030, 1974.
- ◆ A S Bamzai and B M Deb. *Rev. Mod. Phys.* Vol. 53, 95, 593, 1981.
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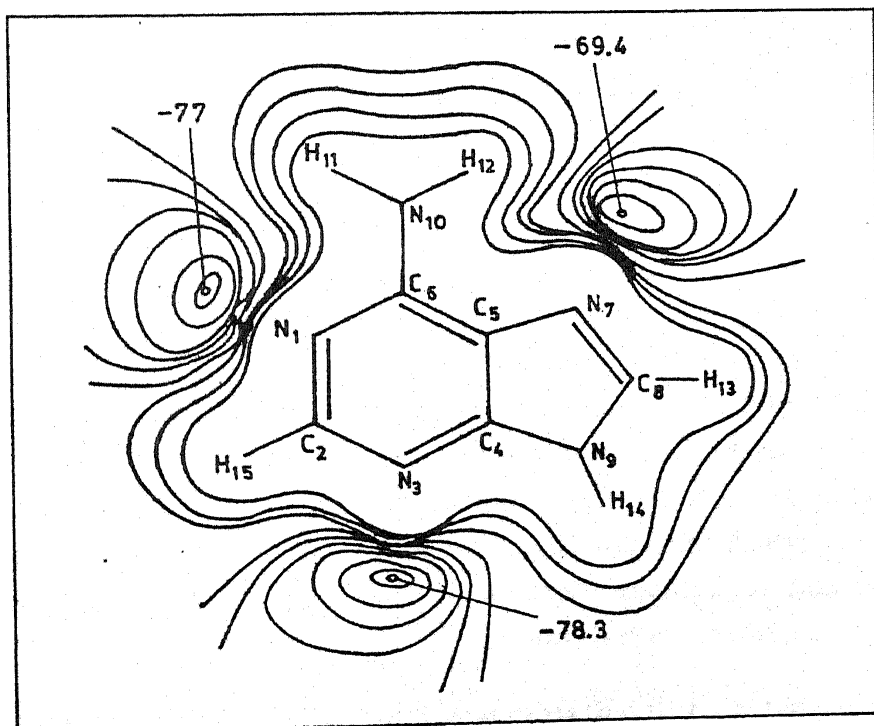


Figure 7. Contours of electrostatic potential in the plane of adenine molecule. The three numbers denote the depths of the minima near N_1 , N_3 and N_7 in kcal mol⁻¹.

Box 2

Apart from other excellent books, there are three classic books on the electronic theory of valence: (1) G N Lewis, *Valence and the Structure of Atoms and Molecules* (1923); (2) L Pauling, *The Nature of the Chemical Bond* (1939); and (3) C A Coulson, *Valence* (1952). Lewis's book popularized the electron-dot structures in chemistry, which evolved from his seminal paper *J. Am. Chem. Soc.* Vol. 38, 762 (1916), published soon after Bohr's theory of the H atom. Pauling's book popularized the quantum-mechanical valence-bond-resonance approach in chemistry while Coulson's book did the same for the molecular-orbital approach.

Reportedly, Lewis was disinclined to take undergraduate classes but was a great inspiration to the graduate students through his seminars and discussions. Pauling is widely regarded as the greatest chemist of this century, who worked in both theoretical and experimental chemistry with equal felicity. As a graduate student, he once wrote to his former teacher that he loved quantum mechanics and statistical mechanics, and thought that the future conceptual framework of chemistry would evolve out of these but his classmates did not think so. Coulson was a mathematician who, apart from R S Mulliken, contributed the most to molecular orbital theory. He did some work in bacteriology besides occupying chairs in mathematics, physics and chemistry. He was once addressed as "Professor of Theological Physics".

R S Mulliken's contributions to molecular orbital theory were numerous and far-reaching, so much so that he was called "Mr Molecule". Reportedly, he had a passion for collecting rugs woven by the Navajo tribe of Red Indians. Another pioneer, J C Slater, who gave the determinantal form to the orbital wavefunction, was once about to be tipped as a hotel boy because he had transported some delegates of a conference to their hotel and carried their luggage himself (next day, the delegates found the "hotel boy" delivering the inaugural address of the conference).

The examples discussed in this article have highlighted the fundamental role played by the electron density in chemistry. Obviously, one would ask : *How does one obtain $\rho(\vec{r})$?* In principle, one may obtain $\rho(\vec{r})$ experimentally by, eg. X-ray diffraction in single crystals. Quantum mechanically $\rho(\vec{r})$ may be calculated either from the molecular wave function or, better, by suitable direct methods which would bypass the wave function and perhaps the Schrödinger equation as well. One should also be able to calculate the dynamical $\rho(\vec{r}, t)$ for an interacting system, where t is real time.

But, that is a different story which needs to be told separately.

Address for Correspondence

B M Deb*

Theoretical Chemistry Group
Department of Chemistry
Panjab University
Chandigarh 160 014, India

*Also at the JNCASR
Bangalore 560 0064, India