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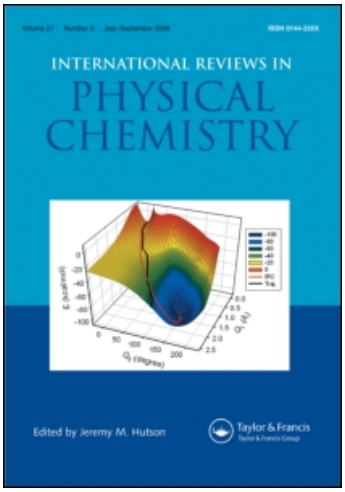

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G. G. Hall[a]
[a] Division of Molecular Engineering, Kyoto University, Kyoto, Japan

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Point charges and the molecular electrostatic potential

by G. G. HALL
Division of Molecular Engineering, Kyoto University,
Kyoto 606, Japan

The topological features of the bare nuclei potential are described in detail. The significance of the impossibility of it having a minimum is discussed. The molecular electrostatic potential and its representation using point charges is then described. The need to have some charges off the nuclei to represent lone pairs and bent bonds is emphasized

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1. Introduction

The concept of a point charge has a long history in the classical theory of electricity and magnetism. It is an obvious model for a very localized charge. It is most successful as a model of a charged conducting sphere since, according to Gauss's theorem, the potential outside is exactly the same as that of a point charge at its centre. On the other hand, difficulties do arise. The point charge has an infinite self-energy and this gives an unwelcome singularity in the total field energy. The significance of the point charge is only partly as a model of a localized charge. It also gives a physical interpretation of the Green's function and, in this role, provides many useful results.

Molecular quantum mechanics uses point charges freely and needs to refine them only very occasionally. In the molecular Hamiltonian both nuclei and electrons are point charges and in most applications are well behaved. An exception is the Fermi contact term which diverges in second-order perturbation theory unless the nucleus is given a finite size (Blinder 1984).

This paper is concerned with point charges in a slightly different sense. Here they are used to represent the electron charge distribution rather than the electron itself. Unfortunately this raises the classical problem of isolating the divergent results from the useful ones. There are many approaches to the problem of deriving point charge models and some will be described and compared in later sections.

The following section discusses the nuclear charges and their potential and uses differential topology to show a limitation on the form of the potential. The third section discusses the molecular electrostatic potential in general and its representation using point charges. In the fourth section some techniques of deriving point charge models are reviewed and in the final section the broader significance of these models is emphasized. Two appendices describe mathematical results used in the earlier sections.

2. The bare nuclei potential

The bare nuclear charges produce a potential which is significant for a molecule since, multiplied by the electron charge, it is the one-particle potential energy term in the Born–Oppenheimer Hamiltonian. It is interesting to investigate the topology of this bare-nuclei potential. The topology of such three-dimensional scalar fields has been discussed in relation to the electron density (Collard and Hall 1977, Bader *et al.* 1979 a, b). The same features are found here. In particular, the type and location of the

critical points, where the first derivatives are zero, are of major importance in characterizing the shape of the potential.

A single point charge has a Coulomb potential

$$\varphi = Z/r, \quad Z > 0$$

which satisfies the Laplace equation everywhere except at the origin $r=0$. In other words, it satisfies the Poisson equation

$$\nabla^2 \varphi = -4\pi Z \delta(\mathbf{r})$$

The form of this potential is simple. It has an infinite maximum at the position of the charge; it remains positive everywhere and it approaches the value 0 at large distances. Since its first derivatives are never all zero it has no critical points but has a maximum at the origin as if the origin were one.

The potential for a diatomic molecule is obtained by adding two such potentials together. It will have infinite maxima at the two nuclei and will fall to zero at large distances. There will also be a critical point on the internuclear axis since the two repulsive fields will balance at one point on this line. At this point the potential will be a minimum relative to other points on the axis but it will be a maximum relative to points in the plane normal to this axis. This is a saddle point (or Col) of type (3, -1) similar to that in the electron density of a diatomic molecule.

When a third nucleus is added the potential becomes more complicated. There are still maxima, one at each nucleus. Between each pair of nuclei the Col where the fields of the two cancel must be moved to the inside of the triangle formed by the nuclei in order to balance the three repulsions. In general there will be three of these Cols, one for each nuclear pair. Consider now the triangle formed by the Cols. The potential must decrease from each Col towards the inside of this triangle and so must have a minimum at some interior point. This critical point will be a minimum in this plane but a maximum in relation to points on the normal to the plane so it will be a saddle point (or col) of type (3,1) similar to the ring saddle point in the electron density.

Before generalizing these results another argument must be included. At a critical point the shape of the surface is determined by the matrix of second derivatives, the Hessian matrix. The principal curvatures of the surface are the eigenvalues of the Hessian. When the three curvatures are positive the point is a minimum and when all are negative it is a maximum. A Col has two negative and one positive curvatures while the col has one negative and two positives. Except at the nuclei, the potential satisfies the Laplace equation and hence the sum of the curvatures is zero. Thus there cannot be a minimum critical point and maxima occur only at the nuclei because there the sum is negative as can be seen from the Poisson equation.

When there are four nuclei, not lying in a plane, the potential becomes very interesting. Consider first three charges. As above, there will be maxima at the nuclei, three Cols inside the triangle and a ring col inside these. As the fourth nucleus is added it will add a repulsion at each of these critical points and the Cols will move towards it to counter this repulsion. The ring col will also move to the inside of the tetrahedron formed by the nuclei. Each of the four faces of this tetrahedron may have a similar set of critical points. For the electron density it is argued that the four ring cols define a region within which the density decreases to a minimum. There cannot be a minimum for the potential so the critical points must be accounted for in some other way. One possibility is that two critical points may coincide to give a catastrophe point. Thus a minimum coinciding with a col has a zero second derivative in one direction and the rank of the

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Hessian is reduced to two. Coincidences between other critical points are also possible. Whatever coincidence occurs in a particular example it is clear that the potential inside the nuclear tetrahedron must be very flat. This is the equivalent for point charges of Gauss's theorem, that the potential inside a conductor is a constant.

The number of critical points of each type is governed by the Poincaré–Hopf relation. If there are M maxima, m minima, C Cols and c cols then

$$M-C+c-m=1$$

but, since $m=0$, the bare potential has

$$M-C+c=1$$

Thus for one nucleus $M=1$, $C=c=0$ and for two $M=2$, $C=1$, $c=0$. For three nuclei $M=3$, $C=3$ so $c=1$. For four $M=4$, $C\leqslant 6$ so $c\leqslant 3$; but, c would be expected to be 4 so one has coincided with a minimum to give a catastrophe point which does not contribute to this equality. This relation summarizes all the previous argument.

This analysis has one general consequence. It has been suggested by Parr and Berk (1981) that the electron density might be a function of the bare nuclear potential. For this to be true they must have critical points in the same positions. But the electron density can and does have a minimum inside a cage of nuclei and the bare nuclear potential does not. Thus there is a qualitative difference between them. Such a difference has been shown for cubane by Politzer and Zilles (1984) and this argument shows that the result is general.

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3. The molecular electrostatic potential

The electrostatic potential due to the electrons is determined from the integral

$$\varphi(\mathbf{r})=-\int\frac{\rho(\mathbf{s})}{|\mathbf{r}-\mathbf{s}|}\,\mathbf{ds}$$

It has some features in common with the nuclear potential but modified by the change of sign. Thus, it cannot possess a maximum since the sum of the curvatures is positive everywhere. It can have minima and these occur at the nuclei since the electron density is a maximum there. Between two nuclei there will be a col and inside a ring a Col. The role of these two critical points is reversed.

The Molecular Electrostatic Potential (MEP) is the sum of the nuclear and electronic potentials. Because the nuclear term is so large near the nuclei it dominates the MEP there. Thus, the nuclei display maxima and between them the nuclear Col usually wins over the smaller electronic col. In the outer regions the electronic term becomes of greater importance. Many maps of the MEP of molecules have been published (see Bonaccorsi *et al.* (1984) and references within). They show that the sum can produce new critical points such as minima in lone pairs and also in some bent bonds. A theorem which can be used to discuss these is outlined in Appendix A.

4. Techniques for deriving point charges

An effective method of deducing a point charge model from a modern calculated wavefunction is to shrink its Gaussians into delta functions (Hall 1973). In effect this puts a charge on each nucleus equal to its Mulliken population (1935) but the overlap population is divided into many small charges along the internuclear axis. The angle dependence of the atomic density will give rise to extra point dipoles and quadrupoles.

This shrinking does not change the total molecular moments (for a proof see Appendix B). The practical difficulty of this model is the rather large number of small charges it requires, one for each pair of Gaussians on different centres.

A practical method of deducing a point charge model is to use two stages in the calculation (Hall and Smith 1984). In the first stage the molecular electron density, which is a quadratic form in the atomic orbitals and so in the basic Gaussians, is approximated by a linear sum of Gaussians. This can be fitted by the optimization of an appropriate functional. It has been argued that the most suitable choice is the energy of the error in the electric field (Hall 1983). If $\mathbf{E}$ is the true field and $\mathbf{E}^*$ the approximate one then the integral

$$I=\frac{1}{8\pi}\int(\mathbf{E}-\mathbf{E}^*)^2\,d\tau=\frac{1}{8\pi}\int(\nabla\varphi-\nabla\varphi^*)^2\,d\tau$$

measures the error. It is minimized with respect to the positions and sizes of the Gaussians until the error is acceptably small. The result is a compact form for the electron density which may be useful in other connections. The second stage of the calculation shrinks these Gaussians to delta functions.

In locating the point charges there is one important principle. The maxima and minima of the MEP should be reproduced. Since a minimum in the potential can be produced only by placing a negative charge there, the minima in lone pairs and bent bonds will necessitate point charges located there. Failure to do so will result in the divergent multipole expansions of the type studied by Stone (1981).

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5. The wider significance of point charge models

The MEP is the first-order term in a perturbation calculation of the interaction energy of two molecules. The second-order terms are also important in a quantitative sense. Yet this first term has a very strong angular dependence, especially at long and medium distances, which is not found in other terms. Thus, for an understanding of the effect of geometry on a chemical reaction, or on the structure of molecular clusters, this first term is often the vital one. The position of the point charges is an easily visualized means of grasping the angular aspects of the forces. The use of the MEP in molecular recognition has been reviewed by Hadzi *et al.* (1984).

The MEP has another important function. The electrical force is the only one which can be reversed. If, when a reaction takes place, the charges are greatly changed then the attraction that brought the molecules together can be turned into a repulsion preventing them form reacting backwards. No other force can be reversed in this way. This can be an important aspect of certain biological reactions and argues that point charge models should be studied as a function of the reaction coordinate.

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Appendix A

If ρ is a charge density and φ the related potential and if a sphere is taken with radius R and centre $\mathbf{c}$ then the average of the potential over the surface of the sphere is given by

$$\bar{\varphi}=\frac{1}{R}\int_{\text{inside}}\rho(\mathbf{s})\,\mathbf{ds}+\int_{\text{outside}}\rho(s)/|\mathbf{c}-\mathbf{s}|\,\mathbf{ds}$$

This is proved by expanding the potential around the point $\mathbf{c}$ and noting that every term vanishes under spherical averaging except the first.

This can be applied to any neutral molecule, with some internal point for $\mathbf{c}$ and a large R, to show that the average potential tends to its asymptotic value of zero from positive values. A molecule with a large dipole may, of course, have some directions along which it tends to zero through negative values.

It also applies to an electronegative atom in a molecule, with $\mathbf{c}$ at its nucleus, and shows that there is a radius such that the total enclosed charge is zero and the first term vanishes while the second is rather small. The average may then go negative outside this sphere. If the potential is negative anywhere then, by continuity of the potential, it must have a minimum value and the potential has a minimum critical point.

Appendix B

If ρ is an electron density which is a linear sum of normalized Gaussians $G_i(\mathbf{r}-\mathbf{p}_i)$ at points $\mathbf{p}_i$

$$\rho=\sum_i q_i G_i(\mathbf{r}-\mathbf{p}_i),\quad \text{where } G_i(\mathbf{r}-\mathbf{p}_i)=(\alpha_i/\pi)^{3/2}\exp\left[-\alpha_i(\mathbf{r}-\mathbf{p}_i)^2\right],$$

then many molecular properties are defined as integrals over the density with an analytic function $M(x,y,z)$. These can be evaluated by two changes of variable, of which the first is

$$\bar{M}\equiv\int\rho(\mathbf{r})M(\mathbf{r})\,\mathbf{dr}=\sum_i q_i\int G_i(\mathbf{r}-\mathbf{p}_i)M(\mathbf{r})\,\mathbf{dr}=\sum_i q_i\int G_i(\mathbf{r})M(\mathbf{r}+\mathbf{p}_i)\,\mathbf{dr}$$

Now as M is analytic it satisfies the Taylor theorem viz.

$$M(\mathbf{r}+\mathbf{p}_i)=\exp\left(\mathbf{r}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right)M(\mathbf{p}_i)$$

so the integral becomes

$$\bar{M}=\sum_i q_i\int G_i(\mathbf{r})\exp\left(\mathbf{r}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right)\mathbf{dr}\,M(\mathbf{p}_i).$$

The second change of variable is

$$G_i\left(\mathbf{r}-\frac{1}{2\alpha_i}\frac{\partial}{\partial\mathbf{p}_i}\right)=(\alpha_i/\pi)^{3/2}\exp\left[-\alpha_i\left(\mathbf{r}^2-\frac{1}{\alpha_i}\mathbf{r}\cdot\frac{\partial}{\partial\mathbf{p}_i}+\frac{1}{4\alpha_i^2}\frac{\partial^2}{\partial\mathbf{p}_i^2}\right)\right]$$

and so $\bar{M}$ has the value

$$\bar{M}=\sum_i q_i\int G_i\left(\mathbf{r}-\frac{1}{2\alpha_i}\frac{\partial}{\partial\mathbf{p}_i}\right)\mathbf{dr}\exp\left(-\frac{1}{4\alpha_i}\frac{\partial^2}{\partial\mathbf{p}_i^2}\right)M(\mathbf{p}_i)=\sum_i q_i\exp\left(-\frac{1}{4\alpha_i}\frac{\partial^2}{\partial\mathbf{p}_i^2}\right)M(\mathbf{p}_i)$$

since the Gaussian remains normalized. This is another version of the proof given by Martin and Hall (1981).

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This is applied to the molecular multipole moments by noting that, for these, each M satisfies the Laplace equation, $\nabla^2 M = 0$, so that the expression reduces to

$$\bar{M} = \sum_i q_i M(\mathbf{p}_i)$$

which is exactly the point charge value.

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