9
Charge Distribution and Spectroscopic Properties

9.1 Properties Related to Charge Distribution

We know from the fundamental theorems of DFT that the charge distribution (i.e., the density) determines the external potential, and that this determines the Hamiltonian operator, and that this in turn ultimately determines the wave function. So, in a formal sense, one might say that the charge distribution determines all molecular properties. For purposes of presentation, however, we will distinguish between properties that are rather direct measures of the charge distribution, and others, such as rotational and vibrational frequencies, that may be regarded as being decoupled from the charge distribution except to the extent that the molecular potential energy surface is intimately connected with it.

This chapter concerns itself with the prediction of a variety of measurable spectroscopic properties, including molecular multipole moments and polarizabilities, electron spin resonance (ESR) hyperfine coupling constants, nuclear magnetic resonance (NMR) chemical shifts and spin–spin coupling constants, and molecular rotational, vibrational, and photoelectron spectra. Because the modeling of electronic spectroscopy — the prediction of energy separations and transition probabilities between distinct electronic states — is somewhat more complex than these others in implementation, its discussion is deferred until Chapter 14. In addition, some ‘unmeasurable’ properties are examined, the most important of which, because it forms the basis for much chemical reasoning, is the concept of partial atomic charge.

9.1.1 Electric Multipole Moments

In Cartesian coordinates, the expectation values of multipole moment operators are computed as

$$
\langle x^k y^l z^m \rangle = \sum_{i} Z_i x_i^k y_i^l z_i^m \psi(r) \left( \sum_j x_j^k y_j^l z_j^m \right) \psi(r) dr
$$

(9.1)
where the sum of $k$, $l$, and $m$ determines the type of moment (0 = monopole, 1 = dipole, 2 = quadrupole, etc.). $Z_i$ is the nuclear charge on atom $i$, and the integration variable $r$ contains the $x$, $y$, and $z$ coordinates of all of the electrons $j$. When $\Psi$ is expressed as a single Slater determinant, we may write

$$\langle x^k y^l z^m \rangle = \sum_i^{\text{atoms}} Z_i x_i^k y_i^l z_i^m - \sum_j^{\text{electrons}} \int \psi_j(r_j) (x_j^k y_j^l z_j^m) \psi_j(r_j) dr_j$$

(9.2)

where $\psi_j$ and $r_j$ are the molecular orbital occupied by electron $j$ and its Cartesian coordinate system, respectively. Equation (9.2) is also valid for DFT, where the various $\psi$ are occupied KS orbitals. For ease of notation, we will restrict our discussion to situations where Eq. (9.2) holds, but all of the qualitative details we will consider are equally valid within the more general formalism of Eq. (9.1).

The simplest moment to evaluate is the monopole moment, which has only the component $k = l = m = 0$, so that the operator becomes 1 and, independent of coordinate system, we have

$$\langle 1 \rangle = \sum_i^{\text{atoms}} Z_i - \sum_j^{\text{electrons}} \int \psi_j(r_j) \psi_j(r_j) dr_j$$

$$= \sum_i^{\text{atoms}} Z_i - N$$

(9.3)

where $N$ is the total number of electrons (the simplification of the second term on the r.h.s. follows from the normalization of the MOs). The monopole moment is thus the difference between the sum of the nuclear charges and the number of electrons, i.e., it is the molecular charge.

For the dipole moment, there are three possible components: $x$, $y$, or $z$ depending on which of $k$, $l$, or $m$ is one (with the others set equal to zero). These are written $\mu_x$, $\mu_y$, and $\mu_z$. Experimentally, however, one rarely measures the separate components of the dipole moment, but rather the total magnitude, $\mu$, which can be determined as

$$\langle \mu \rangle = \sqrt{\langle \mu_x^2 \rangle + \langle \mu_y^2 \rangle + \langle \mu_z^2 \rangle}$$

(9.4)

The dipole moment measures the degree to which positive and negative charge are differentially distributed relative to one another, i.e., overall molecular polarity. Thus, for instance, if the electronic wave function has a large amplitude at some positive $x$ value while the nuclear charge is concentrated at some negative $x$ value, inspection of Eq. (9.2) indicates that the dipole moment in the $x$ direction will be negative. If they are both concentrated at the same position and the total electronic charge is equal to the total nuclear charge, the first and second terms on the r.h.s. of Eq. (9.2) cancel, and the dipole moment is zero. Figure 9.1 illustrates the concept for the case of the water molecule. The nuclear charges are shown here lying flat in the $xy$ plane, and entirely at the nuclear positions. The electrons of the
hydrogen atoms, however, are pulled to the positive \( x \) direction relative to the H nuclei by bonding interactions with the more electronegative O atom (the polarization is exaggerated here by depicting the \( \sigma \) orbitals with surfaces that fail to encompass the nuclear positions). In addition, the oxygen atom contributes two electrons into its in-plane lone pair, the orbital for which is localized at large, positive values of \( x \), while only contributing a single electron each to the \( \sigma \) orbitals, resulting in another net polarization of negative charge in the positive \( x \) direction. The sum of these and other effects is such that water has a dipole moment of 1.8 D in the direction indicated (parallel with the \( x \) axis by symmetry). Note that the out-of-plane \( p \) orbital may be thought of as ‘cancelling’ two protons in the oxygen nucleus when the dipole moment is computed, since it is circularly symmetric about the nucleus when projected into the \( xy \) plane. (Since it is also symmetric above and below the \( xy \) plane, as are all other orbitals, there is no \( z \) component to the dipole moment.)

Note that, if the total number of electrons is equal to the total nuclear charge, then the dipole moment is independent of the choice of origin. This is again fairly obvious from inspection of Eq. (9.2), since any change in origin will affect the total contribution of the first term on the r.h.s. by the same amount as the second term, and the terms have opposite sign; thus, so long as the sum of the atomic numbers is equal to the number of the electrons the net effect of moving the origin is zero. However, if it is not the case that the two are equal, i.e., the system carries a positive or negative charge, then the dipole moment is not independent of origin, since moving it will cause a larger change in the magnitude of the first term on the r.h.s. compared to the second for cations, and of the second term compared to the first for anions. One can show in general that only the first non-zero electric moment of a molecule is independent of origin. For a charged molecule, this is the monopole, for a neutral molecule, the dipole, for a neutral molecule with zero dipole moment (perhaps by symmetry, e.g., \( \text{CO}_2 \)), it is the quadrupole, etc. Any other, higher moment that is reported from a calculation must specify the origin that was chosen in order to be meaningful. The most common choices are the center of charge and the center of mass.

Electrical moments are useful because at long distances from a molecule the total electronic distribution can be increasingly well represented as a truncated multipole expansion, and thus molecular interactions can be approximated as multipole–multipole interactions (charge–charge, charge–dipole, dipole–dipole, etc.), which are computationally particularly
simple to evaluate. At short distances, however, the multipole expansion may be very slowly convergent, and the multipole approximation has less utility.

### 9.1.2 Molecular Electrostatic Potential

A (truncated) multipole expansion is a computationally convenient single center formalism that allows one to quantitatively compute the degree to which a positive or negative test charge is attracted to or repelled by the molecule that is being represented by the multipole expansion. This quantity, the molecular electrostatic potential (MEP), can be computed exactly for any position \( \mathbf{r} \) as

\[
V_{\text{MEP}}(\mathbf{r}) = \sum_{k} Z_k \frac{1}{|\mathbf{r} - \mathbf{r}_k|} \int \frac{\Psi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \Psi(\mathbf{r}') d\mathbf{r}'
\]

(9.5)

Note that this assumes no polarization of the molecule in response to the test charge. The MEP is an observable, although in practice it is rather difficult to design appropriate experiments to measure it. Computationally, it is usually evaluated within the formalism of either HF or DFT theories, in which case one may write

\[
V_{\text{MEP}}(\mathbf{r}) = \sum_{k} Z_k \frac{1}{|\mathbf{r} - \mathbf{r}_k|} - \sum_{\alpha, \beta} P_{\alpha\beta} \int \frac{\psi_{\alpha}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{\beta}(\mathbf{r}') d\mathbf{r}'
\]

(9.6)

where \( \gamma \) and \( s \) run over the indices of the AO basis set, \( P \) is the one-electron density matrix defined by Eq. (4.57) or its appropriate analog for UHF and DFT, and the orbitals \( \psi \) are those comprising the basis set.

The MEP is particularly useful when visualized on surfaces or in regions of space, since it provides information about local polarity. Typically, after having chosen some sort of region to be visualized, a color-coding convention is chosen to depict the MEP. For instance, the most negative potential is assigned to be red, the most positive potential is assigned to be blue, and the color spectrum is mapped to all other values by linear interpolation. If this is done on the molecular van der Waals surface, one can immediately discern regions of local negative and positive potential, which may be informative for purposes of predicting chemical reactivity. Figure 9.2 provides an example of this procedure for a particular example.

### 9.1.3 Partial Atomic Charges

A very old concept in chemistry is to associate molecular polarity with charge build-up or depletion on the individual atoms. In rationalizing hydrogen bonding in water, for instance, we speak of the oxygen being 'negative' and the hydrogen atoms 'positive'. Part of the driving force for this concept is that it allows one to conveniently ignore the wave character of the electrons and deal only with the pleasantly more particulate atoms, these atoms reflecting electronic distribution by the degree to which they carry positive or negative charge.
9.1 PROPERTIES RELATED TO CHARGE DISTRIBUTION

![Chemical Structure](image)

Figure 9.2 MEP of the radical anion produced by one-electron reduction of the dinitroaromatic shown at left. The spectrum is mapped so that red corresponds to maximum negative charge density and deep blue to minimum (here shown in grayscale). This depiction indicates that the buildup of negative charge density is larger on the nitro group ortho to the amino group than on that para to NH₂. Such polarization is consistent with the observed reactivity of the molecule under reducing conditions (Barrows et al. 1996)

Absolutely critical to the efficiency of most force-field methodologies is that they compute electrical interactions as atom-centered charge–charge interactions, so the development of methods for assigning accurate partial charges to atoms in molecules has seen considerable research.

The concept of a partial atomic charge, however, is ill defined. One often sees it written that the atomic partial charge is not a quantum mechanical observable. This is, however, a bit misleading. One *can* define unambiguous procedures making use of well-defined quantum mechanical operators for computing the partial atomic charge, and such procedures are in principle subject to experimental realization (e.g., the atoms-in-molecules charges defined in Section 9.1.3.3). However, there is no universally agreed upon ‘best’ procedure for computing partial atomic charge. This failure to agree is, in some sense, inevitable, because partial atomic charges are used in different ways within the context of different quantitative and qualitative models in chemistry, so there is no reason to expect a single procedure for determining such charges to be optimal for all purposes. Thus, many methodologies have been promulgated for computing partial charges, and we will examine the most prevalent ones here. For taxonomical purposes, it is helpful to categorize different partial charge methodologies into four classes, and the remainder of this section will be subdivided along these lines.

9.1.3.1 Class I charges

A Class I charge is one which is not determined from quantum mechanics, but through some arbitrary or intuitive approach. For instance, in a neutral diatomic molecule having a known dipole moment, one atomic charge must be $+q$ and the other, to preserve charge balance, must be $-q$. One obvious choice for $q$ will be that value that, in conjunction with the experimental bond length $r_e$, causes the classical dipole moment $qr_e$ to be equal to the experimental one.

A less limited Class I charge model that has seen extensive use is the electronegativity equalization model of Rappé and Goddard (1991). In this case, charge is distributed from
atoms to their bonded partners in a manner that is dependent on their Pauling electronegativities and bond orders. This model is especially convenient for molecular mechanics simulations where it is desirable that the partial atomic charges be able to change as a function of a variable local environment.

9.1.3.2 Class II charges

Class II charge models involve a direct partitioning of the molecular wave function into atomic contributions following some arbitrary, orbital-based scheme. The first such scheme was proposed by Mulliken (1955), and this method of population analysis now bears his name. Conceptually, it is very simple, with the electrons being divided up amongst the atoms according to the degree to which different atomic AO basis functions contribute to the overall wave function. Starting from the expression used for the total number of electrons in Eq. (9.3), and expanding the wave function in its AO basis set, we have

\[
N = \sum_{j}^{\text{electrons}} \int \psi_j(\mathbf{r}_j)\psi_j(\mathbf{r}_j)d\mathbf{r}_j
\]

\[
= \sum_{j}^{\text{electrons}} \sum_{r,s} c_{jr}\psi_r(\mathbf{r}_j)c_{js}\psi_s(\mathbf{r}_j)d\mathbf{r}_j
\]

\[
= \sum_{j}^{\text{electrons}} \left( \sum_{r} c_{jr}^2 + \sum_{r \neq s} c_{jr}c_{js}S_{rs} \right)
\]  

(9.7)

where \( r \) and \( s \) index AO basis function \( \psi \), \( c_{jr} \) is the coefficient of basis function \( r \) in MO \( j \), and \( S \) is the usual overlap matrix element defined in Eq. (4.18).

From the last line of Eq. (9.7), we see that we may divide the total number of electrons up into two sums, one including only squares of single AO basis functions, the other including products of two different AO basis functions. Clearly, electrons associated with only a single basis function (i.e., terms in the first sum in parentheses on the r.h.s. of the last line of Eq. (9.7)) should be thought of as belonging entirely to the atom on which that basis function resides. As for the second term, which represents the electrons 'shared' between basis functions, Mulliken suggested that one might as well divide these up evenly between the two atoms on which basis functions \( r \) and \( s \) reside. If we follow this prescription and furthermore divide the basis functions up over atoms \( k \) so as to compute the atomic population \( N_k \), Eq. (9.7) becomes

\[
N_k = \sum_{j}^{\text{electrons}} \left( \sum_{r \neq k} c_{jr}^2 + \sum_{r \neq k, s \neq k} c_{jr}c_{js}S_{rs} \right)
\]  

(9.8)

Note that those cases where \( r \) and \( s \) are different AO basis functions both residing on \( k \) drop out because the orthonormality of the atomic basis functions on a single center makes all the corresponding overlap integrals zero. The Mulliken partial atomic charge is then defined as
where $Z$ is the nuclear charge and $N_k$ is computed according to Eq. (9.8).

With minimal or small split-valence basis sets, Mulliken charges tend to be reasonably intuitive, certainly in sign if not necessarily in magnitude. Analysis of changes in charge as a function of substitution or geometric change tends to be the best use to which Mulliken charges may be put, and this can often provide chemically meaningful insight, as illustrated in Figure 9.3.

The use of a non-orthogonal basis set in the Mulliken analysis, however, can lead to some undesirable results. For instance, if one divides up the total number of electrons over AO basis functions (in a fashion exactly analogous to that used for atoms), it is possible for individual basis functions to have occupation numbers greater than 1 (which would be greater than 2 in a restricted theory) or less than 0, and such a situation obviously can have no physical meaning. In addition, the rule that all shared electrons should be divided up equally between the atoms on which the sharing basis functions reside would seem to ignore the possibly very different electronegativities of these atoms. Finally, Mulliken partial charges prove to be very sensitive to basis-set size, so that comparisons of partial charges

![Graph](image_url)

**Figure 9.3** AM1 Mulliken charges of the hydroxyl (circles) and oxonium (squares) oxygen atoms in protonated dihydroxymethane as a function of HO\textsubscript{CO} \textsuperscript{+} dihedral angle. Standard precepts of conformational analysis suggest that hyperconjugation of hydroxyl oxygen lone-pair density (acting as a donor) into the C=O \textsuperscript{+} \sigma^* orbital (acting as an acceptor) may occur, and the effect is expected to be maximal at a dihedral angle of 90°, and minimal at 0° and 180°. The computed Mulliken charges on the oxygen atoms support hyperconjugation being operative, with about one-tenth of a positive charge being transferred from the oxonium oxygen to the hydroxyl oxygen at a dihedral angle of 90° compared to 180° (an interpretation also consistent with geometric and energetic analysis, see Cramer 1992)
from different levels of theory are in no way possible. Moreover, with very complete basis sets, Mulliken charges have a tendency to become unphysically large.

To alleviate a number of these problems, Löwdin proposed that population analysis not be carried out until the AO basis functions $\psi$ were transformed into an orthonormal set of basis functions $\chi$ using a symmetric orthogonalization scheme (Löwdin 1970; Cusachs and Politzer 1968)

$$\chi_r = \sum_s S_{rs}^{-1/2} \psi_s$$  \hspace{1cm} (9.10)

where $r$ and $s$ run over the total number of basis functions, and $S^{-1/2}$ is the inverse of the square root of the overlap matrix. When the MOs $\phi$ are expressed in the new orthonormal basis set, the result is

$$\phi_j = \sum_r a_{jr} \chi_r$$

$$= \sum_r \sum_s S_{rs}^{1/2} c_{jr} \chi_r$$  \hspace{1cm} (9.11)

where the new coefficients $a_j$ can be easily determined from the old coefficients $c$. Note that Mulliken analysis applied with the adoption of the orthogonalized basis set has no problem with shared electrons, because the overlap matrix in the new basis set is the unit matrix, so every term in the second sum on the r.h.s. of Eq. (9.8) is zero.

Löwdin population analysis enjoys much better stability than Mulliken analysis in terms of the predicted atomic partial charges as a function of basis set. For instance, the Mulliken charge on the central carbon atom of the allenyl anion (C$_3$H$_3^-$) changes from $-0.17$ at the HF/3-21G level to 2.47 when diffuse functions are added to the basis set. By contrast, the Löwdin charge changes only from $-0.09$ to $-0.21$. Nevertheless, even Löwdin charges can eventually become unstable with very large basis sets.

The shortcoming in the Löwdin procedure derives from the symmetric nature of the orthogonalization. In a very large basis set, only a few AOs are really very important, but in the Löwdin process all AOs are distorted in a similar fashion to achieve orthonormality. A considerably more complicated procedure for achieving orthogonality is used in the Natural Population Analysis (NPA) scheme of Reed, Weinstock, and Weinhold (1985). Ignoring the exact details, orthogonalization takes place in a four-step process in such a way that the electron density around each atom is initially rendered as compact as possible, and further diagonalization is carried out so as to preserve the shape of the strongly occupied atomic orbitals to as large an extent as possible. Following orthogonalization, again, a Mulliken-like analysis in the new basis gives the atomic populations with no contributions from off-diagonal terms.

The most appealing feature of the NPA scheme is that each atomic partial charge effectively converges to a stable value with increasing basis-set size. In comparison to other schemes, however, including some of those yet to be discussed, NPA charges tend to be amongst the largest in magnitude, which can be mildly disquieting. However, as with any population
analysis method, a focus on absolute partial atomic charges is usually much less profitable than an analysis of trends in charge(s) as a function of some variable.

Note that all of the Class II charge models discussed here suffer from the disadvantage of their population analyses being orbital-based. To illustrate this point, consider a calculation on the water molecule using an infinite basis, but one with every basis function defined so as to be centered on the oxygen atom. Insofar as the basis set is infinite, we should be able to obtain an arbitrarily good representation of the density, but in this case, Mulliken, Lönndin, and NPA analyses are all equivalent, and all predict that the oxygen atom charge is −2 and the hydrogen atom charges are +1, since all electrons necessarily reside on oxygen, that being the only atom with basis functions. Nevertheless, the great speed with which Class II charges can be computed (Mulliken charges are the fastest, followed by Lönndin, and then by NPA) suggests that they will remain useful tools for qualitative analysis for some time to come.

9.1.3.3 Class III charges

Rather than being determined from an (arbitrary) analysis of the wave function itself, Class III charges are computed based on analysis of some physical observable that is calculated from the wave function. As already noted in Section 9.1.3.1, there is an obvious relationship that may be proposed between atomic partial charges and dipole moments in diatomics. Cioslowski (1989) has generalized this idea for polyatomic molecules, defining the generalized atomic polar tensor (GAPT) charge as

$$q_k = \frac{1}{3} \left( \frac{\partial \mu_x}{\partial x_k} + \frac{\partial \mu_y}{\partial y_k} + \frac{\partial \mu_z}{\partial z_k} \right)$$  (9.12)

where the quantities evaluated on the r.h.s. are the changes in the molecular dipole moment as a function of moving atom $k$ in each of the three Cartesian directions (the GAPT charge is independent of coordinate system).

While GAPT charges converge quickly with respect to basis-set size, it is important to note that a level of theory that fails to give good dipole moments (e.g., HF) is then unlikely to give useful charges. In addition, GAPT charges are relatively expensive to compute – equivalent to the cost of a vibrational frequency calculation, as described in Section 9.3.2.2 – and as such they have seen only moderate use in the literature.

An alternative physical observable that has been used to define partial atomic charges is the electron density. In X-ray crystallography, the electron density is directly measured, and by comparison to, say, spherically symmetric neutral atoms, atomic partial charges may be defined experimentally, following some decisions about what to do with respect to partitioning space between the atoms (Coppens 1992). Bader and co-workers have adopted a particular partitioning scheme for use with electronic structure calculations that defines the atoms-in-molecules (AIM) method (Bader 1990). In particular, an atomic volume is defined as that region of space including the nucleus that lies within all zero-flux surfaces surrounding the nucleus.
To make this more clear, let us consider the electron density more closely. As already noted in Section 8.1.1, local maxima in the density occur at the positions of the nuclei. Now, imagine following some path outwards from the nucleus, where the direction we take is opposite to the gradient of the density. Two possibilities exist and are illustrated in Figure 9.4 for the case of HCN. Either we will proceed outward from the molecule indefinitely, with the density dropping off exponentially but in principle never reaching zero, or, on rare occasions, we will come to a point where the gradient does reach zero, because it passes from a negative value (falling back towards the nucleus we started from) to a positive value (falling towards some other nucleus). These latter points are called ‘bond critical points’ and in AIM theory it is their existence that defines whether a bond between two atoms exists or not. In any case, we may define the zero-flux surface mathematically as the union of all points for which

$$\nabla \rho \cdot n = 0$$  \hspace{1cm} (9.13)

where $\rho$ is the density and $n$ is the unit vector normal to the surface. Note that to satisfy this condition, either the gradient of the density must run along the surface itself (in which case it is orthogonal to the unit vector) or it must be zero (i.e., the density has a critical point). Bond critical points are minima in the density for the direction to and from the two nuclei defining the bond, but maxima for the density within the zero-flux surface itself. Two other kinds of critical points can exist, so-called ‘ring critical points’, which are found in the interiors of rings and are minima in two dimensions but maxima in one, and ‘cage critical points’, which can be found in the middle of polyhedral structures, and are local minima in all directions.

The analysis of bond, ring, and cage critical points, and of the behavior of the electron density in their vicinity, is a subject of considerable interest for the analysis of chemical structure and reactivity, but beyond the scope of this text (interested readers are directed to Bader 1991). For our purposes, we will restrict ourselves to consideration of partial atomic
charge which, within the AIM theory, is defined as nuclear charge less the total number of electrons residing within the atomic basin. That is

\[ q_k = Z_k - \int_{\Omega_k} \rho(\mathbf{r}) d\mathbf{r} \]  

(9.14)

where the integral is marked to indicate that it is over the spatial volume \( \Omega_k \) encompassed by the zero-flux surface of \( k \).

Partial atomic charges from the AIM method are derived from a formalism that is really quite elegant, but in practice they are of little chemical utility. At times, AIM charges can even seem rather bizarre – for instance, saturated hydrocarbons are predicted to have weakly positive carbon atoms and weakly negative hydrogen atoms, in disagreement with essentially every other method for assigning partial atomic charges. This odd behavior does not derive from any particular flaw within the methodology, but more from it being inconsistent with the purpose to which partial charges are usually meant to be put. The problem is that the charge within an atomic basin may be very non-uniformly distributed, as illustrated in Figure 9.5 for the methyl diazonium cation. In such an instance, the electron density may be 'piled up' rather far from the nucleus, but Eq. (9.14) does not distinguish that situation from the charge being spherically symmetric about the nucleus. In Figure 9.5, the polarization of the molecule is such that the electronic charge associated with the basin of the terminal nitrogen localizes predominantly in the region labeled \( a \), while there is proportionately much less in the region labeled \( b \). Thus, there is a rather large local dipole moment associated with this basin. This dipole is not well represented when only partial atomic charges are considered and the partial atomic charge itself is obtained by simply summing the total density in the basin with the nuclear charge. Moreover, the position of the zero-flux surface between two identical atoms (e.g., the two nitrogen atoms) is very sensitive to their substitution, since they otherwise have equal electronegativities. Small movements of the surface (e.g., when

Figure 9.5  AIM partitioning of space in a plane containing four atoms of \( \text{CH}_3\text{N}_2^+ \) (the other two hydrogen atoms are symmetrically above and below the plane)
methyl is changed to ethyl) can cause large changes in the total density assigned to each basin, even though the density itself does not change much. This leads to unphysically large changes in partial atomic charge that are simply artifacts if higher electrical moments in the basins are not also taken into consideration.

The solution to this problem is to compute not simply the AIM charges, but also atomic multipole moments (defined over the atomic basins in a fashion analogous to their definition over all space for molecules). However, while this provides an accurate picture of the electron density distribution, it is inconsistent with the simplification that is the goal of using only partial atomic charges in the first place. As a rule, then, AIM partial atomic charges should not be used for analysis without some indication that the lower atomic multipole moments are quantitatively unimportant. As the necessary determinations of atomic volumes and the integrations over them are time-consuming, AIM analysis is not a routine undertaking.

The final observable from which charges are typically derived is the MEP. In the field of partial charges, the more common notation is to replace MEP with ESP, for ‘electrostatic potential’ (and not ‘extrasensory perception’), and we will follow that convention from this point on. The ESP is perhaps the most obvious property to reproduce if one wants partial atomic charges that will be useful in modeling molecule–molecule interactions at short to long range, as is the case, say, in molecular mechanics simulations (Williams 1988). All ESP charge-fitting schemes involve determining atomic partial charges \( q_k \) that, when used as a monopole expansion according to

\[
V_{\text{ESP}}(\mathbf{r}) = \sum_{k} \frac{q_k}{|\mathbf{r} - \mathbf{r}_k|}
\]  

(9.15)

minimize the difference between \( V_{\text{ESP}} \) and the correct \( V_{\text{MEP}} \) calculated according to Eq. (9.5). Typical algorithms select a large number of points spaced evenly on a cubic grid surrounding the van der Waals surface of the molecule. To ensure rotational invariance, a reasonable density of points is required. The two algorithms in widest use are CHELPG (Breneman and Wiberg 1990), which is a modification designed to improve the stability of the charges from electrostatic potentials (CHELPG) algorithm of Chirlian and Francl (1987), and the scheme of Besler, Merz, and Kollman (1990), which is sometimes slightly less robust than CHELPG, but usually gives very similar results.

When ESP charges are to be used in molecular simulations for flexible molecules, it is something of a problem to decide what to do about the conformational dependence of the partial charges. Thus, for instance, no more than two of the three methyl hydrogen atoms in methanol are ever symmetrically related for any reasonable conformation, so there will always be at least two different hydrogen partial atomic charges. Since the methyl group is freely rotating in a simulation, however, it is unreasonable to distinguish between the hydrogens. A modification of the ESP method advanced by Cornell et al. (1995) to address this issue is the restrained ESP (RESP) approach, where such dilemmas are erased by fiat. Of course, if resources permit, a more accurate simulation can take account of the conformational dependence of partial atomic charges, but such a protocol is very rarely adopted.
since it is not only intrinsically expensive, but complicates force-field energy derivatives enormously. One compromise solution is to use fixed partial charges that are adjusted to reflect some weighted average over accessible conformations (see, for example, Basma et al. 2001).

A more serious problem with ESP methods is that the resulting partial charges have been shown to be ill conditioned (Francl and Chirlian 2000). That is, the statistical reliability for some or many of the charges may be very low. This problem is particularly true for atoms in molecules that are not near the molecular surface. Wide variations in partial atomic charge for such atoms have minimal impact on the ESP at any point, particularly if the charges for atoms nearer to the surface are allowed to adjust slightly, so the final value from the minimization process is not particularly meaningful (and indeed, numerical instabilities in the fitting procedure may arise in unfavorable cases). While this problem is not necessarily anything to worry about when computing intermolecular interactions within a force-field calculation (if the ESP is insensitive to that partial charge, then so is the interaction energy), to the extent intramolecular interactions are also computed using the ESP charges, problems may develop.

### 9.1.3.4 Class IV charges

A hallmark of Class II and Class III charges is that they are derived from analysis of computed wave functions and physical observables, respectively. Thus, to the extent that an employed level of theory is in error for the particular quantity computed, the partial charges will faithfully reflect that error. A Class IV charge, on the other hand, is one that is derived by a semiempirical mapping of a precursor charge (either from a Class II or Class III model), in order to reproduce an experimentally determined observable.

Charge Model I (CM1) was the first method developed to compute Class IV charges (Storer et al. 1995). In this model, the input charges are Mulliken charges determined at a semiempirical level – different CM1 mappings are available for both the AM1 and PM3 Hamiltonians – and the experimental observable for which the mappings were optimized was the molecular dipole moment as computed from the atomic partial charges according to

\[
\mu = \left[ \left( \sum_k q_k x_k \right)^2 + \left( \sum_k q_k y_k \right)^2 + \left( \sum_k q_k z_k \right)^2 \right]^{1/2}
\]  

(9.16)

The form of the mapping itself is relatively simple, with the CM1 charge defined as

\[
q_k^{\text{CM1}} = q_k^{(0)} B_k \Delta q_k - \sum_{k' \neq k} B_{kk'} \Delta q_{k'}.
\]  

(9.17)

where \(q_k^{(0)}\) is the input Mulliken charge, \(B_{kk'}\) is the bond order between atoms \(k\) and \(k'\), and \(B_k\) is defined as the sum of the bond orders of atom \(k\) to all other atoms. The quantity \(\Delta q_k\)
is where the mapping comes in, and it is computed as

\[ \Delta q_k = c_k q_k^{(0)} + d_k \]  \hspace{1cm} (9.18)

where parameters \( c \) and \( d \) are optimized for each atom \( k \) so as to minimize errors in the predicted dipole moments. The form of Eq. (9.17) is such that (i) charge redistribution is local (since charge is passed between atoms based on the bond order between them) and (ii) total charge is preserved. The bond order is determined, as originally suggested by Mulliken in conjunction with population analysis, as

\[ B_{kk'} = \sum_{\mu \in k} \sum_{\nu \in k'} n_{\mu \nu}^2 \]  \hspace{1cm} (9.19)

The CM1 models for AM1 and PM3 yield root-mean-square errors of 0.30 and 0.26 D, respectively, in the dipole moments of 195 neutral molecules consisting of 103 molecules containing H, C, N, and O covering variations of multiple common organic functional groups, 68 fluorides, chlorides, bromides, and iodides, 15 compounds containing H, C, Si or S, and 9 compounds containing C–S–O or C–N–O linkages. Duffy and Jorgensen have demonstrated the utility of using CM1-AM1 partial atomic charges for arbitrary solutes in force-field simulations (Duffy and Jorgensen 2000).

In later work, Li et al. (1998, 1999) defined the next generation Charge Model 2 (CM2) in an overall analogous fashion, except that the input charges were Löwdin charges instead of Mulliken, the bond orders were determined from the analog of Eq. (9.19) for Löwdin analysis (Mayer 1983), and the parameters were changed from being atom specific to being atom-pair specific. CM2 mappings have been defined for many different levels of theory, including semiempirical, HF, and DFT. The performance of the CM2 models is roughly equivalent to that for the CM1 models, but the reliance on Löwdin charges instead of Mulliken charges makes them more robust when employed for \textit{ab initio} levels of electronic structure theory and when applied to molecules differing greatly from any found in the training set.

Table 9.1 provides several molecular dipole moments as computed by a variety of different charge models and electronic structure methods, and compares them to experiment. The expectation value of the dipole moment evaluated for MP2/6-31G(d) wave functions has an RMS error compared to experiment of 0.2 D. The same expectation value at the HF level shows the expected increase in error from the tendency of the HF level to overestimate dipole moments. Dipole moments computed using Eq. (9.16) and ESP charges have about the same accuracy as the expectation value (indeed, it is possible to constrain the ESP fit so that the expectation value of the dipole moment is exactly reproduced; of course, this is not necessarily desirable if one knows the expectation value to suffer from a systematic error because of the level of theory). Equation (9.16) used with either Mulliken or NPA charges shows rather high errors. At the PM3 level, not only are the Mulliken charges rather bad, but the expectation value of the dipole moment operator is not particularly good either. However, the CM1 mapping corrects for the errors in the PM3 electronic structures sufficiently well that the RMS error for the CM1P model is lower than that for the MP2 expectation value.
Table 9.1 Dipole moments (D) computed from different methods and RMS error compared to experiment

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Expt.</th>
<th>MP2&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HF/6-31G(d)</th>
<th>PM3</th>
<th>AM1</th>
<th>BPW91&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(μ)</td>
<td>(μ)</td>
<td>Mullik.</td>
<td>ESP</td>
<td>NPA</td>
<td>Mullik.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>CM1P</td>
<td>CM1A</td>
<td>CM2</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>1.85</td>
<td>2.16</td>
<td>2.20</td>
<td>2.39</td>
<td>2.25</td>
<td>2.63</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.70</td>
<td>1.77</td>
<td>1.87</td>
<td>2.08</td>
<td>1.85</td>
<td>3.00</td>
</tr>
<tr>
<td>Methyl formate</td>
<td>1.77</td>
<td>1.87</td>
<td>2.04</td>
<td>1.85</td>
<td>2.03</td>
<td>2.24</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>2.33</td>
<td>2.17</td>
<td>2.67</td>
<td>3.15</td>
<td>2.67</td>
<td>3.97</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.88</td>
<td>2.64</td>
<td>3.11</td>
<td>3.80</td>
<td>3.15</td>
<td>4.65</td>
</tr>
<tr>
<td>Cyclopropanone</td>
<td>2.67</td>
<td>2.58</td>
<td>3.15</td>
<td>3.65</td>
<td>3.19</td>
<td>2.43</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>1.70</td>
<td>1.46</td>
<td>1.79</td>
<td>2.00</td>
<td>1.83</td>
<td>2.37</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>1.30</td>
<td>1.50</td>
<td>1.62</td>
<td>2.72</td>
<td>1.63</td>
<td>3.04</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>1.63</td>
<td>1.84</td>
<td>1.95</td>
<td>2.96</td>
<td>1.92</td>
<td>3.36</td>
</tr>
<tr>
<td>Furan</td>
<td>0.66</td>
<td>0.60</td>
<td>0.77</td>
<td>1.96</td>
<td>0.74</td>
<td>1.75</td>
</tr>
<tr>
<td>Ammonia</td>
<td>1.47</td>
<td>1.92</td>
<td>1.92</td>
<td>1.77</td>
<td>1.96</td>
<td>1.98</td>
</tr>
<tr>
<td>Methylamine</td>
<td>1.31</td>
<td>1.50</td>
<td>1.53</td>
<td>1.60</td>
<td>1.48</td>
<td>1.81</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>2.99</td>
<td>2.96</td>
<td>3.21</td>
<td>3.65</td>
<td>3.16</td>
<td>3.08</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>3.93</td>
<td>3.75</td>
<td>4.04</td>
<td>4.75</td>
<td>4.03</td>
<td>3.79</td>
</tr>
<tr>
<td>Formamide</td>
<td>3.73</td>
<td>3.73</td>
<td>4.10</td>
<td>4.27</td>
<td>4.10</td>
<td>5.16</td>
</tr>
<tr>
<td>Acetamide</td>
<td>3.76</td>
<td>3.63</td>
<td>4.03</td>
<td>4.26</td>
<td>4.05</td>
<td>5.21</td>
</tr>
<tr>
<td>Cyanamide</td>
<td>4.32</td>
<td>4.36</td>
<td>4.56</td>
<td>3.91</td>
<td>4.58</td>
<td>3.92</td>
</tr>
<tr>
<td>Fluoromethane</td>
<td>1.86</td>
<td>1.78</td>
<td>1.99</td>
<td>3.41</td>
<td>2.00</td>
<td>3.68</td>
</tr>
<tr>
<td>Methylsilane</td>
<td>0.74</td>
<td>0.72</td>
<td>0.68</td>
<td>0.03</td>
<td>0.66</td>
<td>0.78</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>0.97</td>
<td>1.49</td>
<td>1.41</td>
<td>0.96</td>
<td>1.52</td>
<td>1.14</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>1.52</td>
<td>1.78</td>
<td>1.79</td>
<td>−0.86</td>
<td>1.75</td>
<td>0.71</td>
</tr>
<tr>
<td>Thiophenol</td>
<td>1.65</td>
<td>1.70</td>
<td>2.23</td>
<td>1.64</td>
<td>2.27</td>
<td>0.88</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>1.89</td>
<td>2.08</td>
<td>2.25</td>
<td>1.99</td>
<td>2.30</td>
<td>2.00</td>
</tr>
<tr>
<td>RMS error</td>
<td>0.21</td>
<td>0.31</td>
<td>0.93</td>
<td>0.33</td>
<td>0.33</td>
<td>1.05</td>
</tr>
</tbody>
</table>

<sup>a</sup> MP2/6-31G(d)//HF/6-31G(d).  
<sup>b</sup> BPW91/MIDI//HF/MIDI!

The CM1 model with the AM1 Hamiltonian and the CM2 model for the BPW91/MIDI! level of theory also do well. Note that the CM1 and CM2 models, the last three columns of the table, represent three of the fastest methodologies listed.

9.1.4 Total Spin

Well-behaved wave functions are eigenfunctions of the total spin operator \( S^2 \), having eigenvalues of \( s(s + 1) \), where the quantum number \( s \) is 0 for a singlet, 1/2 for a doublet, 1 for a triplet, etc. One sometimes sees it written that \( s \) is equal to the sum of the \( s_e \) values for all of the electrons, where \( s_e \) is the expectation value of the corresponding operator \( S_z \) (spin angular momentum along the \( z \) coordinate) and takes on values in a.u. of +1/2 for an \( \alpha \) electron and −1/2 for a \( \beta \) electron. This is incorrect, however. In fact, \( s \) is equal to the magnitude of the vector sum of the individual electronic angular momenta, and thus \( s \) can