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Mulliken-Dipole Population Analysis.

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Abstract

Atomic charge is one of the most important concepts in Chemistry. Mulliken population analysis is historically the most important method to calculate atomic charges and is still widely used. One basic hypothesis of this method is the half-and-half partition of the overlap populations, $Q(\mu, \nu)$, into equal charges in orbitals μ and ν . This partition preserves the monopole moment of the overlap density but, other than that, is arbitrary. In this work we derive a new population analysis (which we designate Mulliken-Dipole population analysis) based on the conservation of both the monopole moment and the dipole moment along the bond direction. Test calculations show that the Mulliken-Dipole atomic charges are in accord to the chemical intuition; also they

are very different from the Mulliken ones, being quite similar to the Hirshfeld atomic charges. Mulliken-Dipole atomic charges are conceptually appealing and very easy to calculate. In a further step, we also show how this Mulliken-Dipole population analysis can be used to derive atomic charges for atomistic simulations that reproduce the total dipole moment of the molecule, yielding at the same time a good description of the local charges and dipole moments for the molecular fragments.

Introduction

Atomic charges in materials are a very important tool in Chemistry, Physics and Biology both from the conceptual and the practical points of view.¹⁻¹⁹ For example, the idea of atomic charges is basic in many theories that explain the properties of the materials, and atomic charges are used routinely to interpret experimental data. Also, atomic charges are a fundamental component in atomistic simulations of complex materials using Molecular Mechanics force fields or other approximate methods.

The concept of atomic charge is a very intuitive one (the amount of charge that we can assign to an atom in a molecule, solid or liquid), yet it is not unambiguously defined; thus different approaches have been developed for their calculation. The most famous one is Mulliken population analysis (PA),¹ which was proposed in 1955 and is still widely used, in spite of some well-known deficiencies, due to its calculational simplicity and conceptual appeal. In similarity to Mulliken PA, other methods to calculate atomic charges are based on the density matrix, using a suitable, balanced, basis set of atomic-like orbitals, such as the Löwdin² (L) or the Natural PA³ methods. Alternatively, the atomic charges can be defined via direct integration of the electron density in real space $\rho(\mathbf{r})$ with a prescription on how to split this electron density into different atomic contributions.^{4-6,20-30} For example, in the Quantum Theory of Atoms-in-Molecules (AIM-QT)^{5,6,20} method, the electron density is divided into non-overlapping regions of space around the different atomic positions. In the Hirshfeld (HIR)⁴ (or stockholder) method the electron density at each point in space, $\rho(\mathbf{r})$,

is assigned a relative probability to belong to each atom, probability that is proportional to the value of the neutral atom electron density at that point. The electron density $\rho(\mathbf{r})$ can also be used to determine the electrostatic potential (ESP) of the molecule and then obtain partial atomic charges by fitting, in a given region of space, the ESP due to the partial atomic charges to the ESP due to the electron density $\rho(\mathbf{r})$ and nuclei.^{7-11,31-33} Moreover, with the goal of obtaining atomic charges that yield a good description of the electrostatic interactions, methods have been developed to optimize the description of the molecular dipole moments, introducing variations to the atomic charges initially calculated with one of the methods mentioned above (*e.g.* Mulliken, L, HIR).^{17,18,34-39}

Since atomic charges are used for different purposes, and are not uniquely defined, different methods are better suited for different applications. For example, atomic charges used in force field molecular mechanics simulations should, ideally, represent accurately the total atomic dipole of the molecules, as well as the local charge and dipole moment for their constituent molecular fragments (*e.g.* functional groups). On the other hand, atomic charges used for conceptual understanding should properly reflect the charge variations as a function of the chemical environment.

In this work we derive a new PA method, that we denominate Mulliken-Dipole PA. At variance with Mulliken PA, that is based on the half-and-half partition of each overlap population, the Mulliken-Dipole PA is defined in terms of the two most important physical properties of the overlap densities, *i.e.* their monopole and dipole moments. Test calculations for some selected molecules show that the M-D atomic charges follow the intuitive chemical trends based on the electronegativities of the atoms. The M-D charges are quite different from the Mulliken ones and present an interesting similarity to the HIR charges. We conclude that both M-D and HIR PA are good tools for the conceptual rationalization of chemical processes. Finally, we discuss how the M-D PA can also be used to derive atomic charges that replicate the total dipole moment, appropriately including the effects of the intra-atomic dipoles.³⁷⁻³⁹ Our test calculations show that the resulting atomic charges, which are suited

for atomistic simulations, give values between ESP and CM5 charges.

Electron density and overlap populations.

In this work we represent the electron density $\rho(\mathbf{r})$ as :

$$\rho(\mathbf{r}) = \sum_i f_i |\psi_i(\mathbf{r})|^2 = \sum_{\mu\nu} P_{\nu\mu} \phi_\mu^*(\mathbf{r} - \mathbf{R}_m) \phi_\nu(\mathbf{r} - \mathbf{R}_n), \quad (1)$$

where the orbitals $\phi_\mu(\mathbf{r} - \mathbf{R}_m)$ are a suitable basis set of orbitals centered in the different atoms, m ; \mathbf{R}_m and \mathbf{R}_n are the positions of the atoms m and n : orbital μ belongs to atom m while orbital ν belongs to atom n . $\psi_i(\mathbf{r})$ are the eigenstates (molecular orbitals) that are obtained *e.g.* from a DFT or Hartree-Fock calculation, $\psi_i(\mathbf{r}) = \sum_\mu c_{\mu i} \phi_\mu(\mathbf{r} - \mathbf{R}_m)$, f_i are the occupation factors and $P_{\nu\mu}$ is the density matrix, $P_{\nu\mu} = \sum_i f_i c_{\nu i} c_{\mu i}^*$.

Eq. (1) is a sum of electron densities for each pair of orbitals (μ, ν) :

$$\rho(\mathbf{r}) = \sum_{(\mu, \nu)} \rho(\mu, \nu)(\mathbf{r}) \quad (2)$$

where the sum extends to all the pairs (μ, ν) , with:

$$\rho(\mu, \nu)(\mathbf{r}) = P_{\nu\mu} \phi_\mu^*(\mathbf{r} - \mathbf{R}_m) \phi_\nu(\mathbf{r} - \mathbf{R}_n) + P_{\mu\nu} \phi_\nu^*(\mathbf{r} - \mathbf{R}_n) \phi_\mu(\mathbf{r} - \mathbf{R}_m). \quad (3)$$

Each overlap density $\rho(\mu, \nu)$ yields the following overlap population (or overlap charge):

$$Q(\mu, \nu) = \int \rho(\mu, \nu)(\mathbf{r}) d^3r = (P_{\nu\mu} S_{\mu\nu} + P_{\mu\nu} S_{\nu\mu}), \quad (4)$$

where $S_{\mu\nu} = \int \phi_\mu^*(\mathbf{r} - \mathbf{R}_m) \phi_\nu(\mathbf{r} - \mathbf{R}_n) d^3r$ is the overlap matrix.

In Mulliken PA each $Q(\mu, \nu)$ is *equally* distributed into charges $q_\mu(\mu, \nu)$ and $q_\nu(\mu, \nu)$

corresponding to orbitals μ and ν :¹

$$q_\mu(\mu, \nu) = q_\nu(\mu, \nu) = \frac{Q(\mu, \nu)}{2} = \frac{1}{2} (P_{\nu\mu} S_{\mu\nu} + P_{\mu\nu} S_{\nu\mu}), \quad (5)$$

preserving in this way the monopole moment, eq. (4):

$$q_\nu(\mu, \nu) + q_\mu(\mu, \nu) = (P_{\nu\mu} S_{\mu\nu} + P_{\mu\nu} S_{\nu\mu}). \quad (6)$$

The total electron charge in each orbital is then calculated adding the contributions from all $Q(\mu, \nu)$:

$$q_\mu^M = \sum_\nu \frac{1}{2} (P_{\nu\mu} S_{\mu\nu} + P_{\mu\nu} S_{\nu\mu}) = \frac{1}{2} (\mathbf{S}\mathbf{P} + \mathbf{P}\mathbf{S})_{\mu\mu}; \quad (7)$$

\mathbf{S} and \mathbf{P} are the overlap and density matrices. In most applications the eigenstates ψ_i and basis orbitals ϕ_μ are real, and equation (7) is simplified to $q_\mu^M = \sum_\nu P_{\mu\nu} S_{\nu\mu} = (\mathbf{P}\mathbf{S})_{\mu\mu}$.

Thus, the basic ingredients of Mulliken PA are the linear dependence on the density matrix elements, $P_{\mu\nu}$, together with the preservation of the monopole moment for each overlap density, eq. (6), and the assignment of equal charges, eq. (5). Also, in order to yield meaningful results, the basis set must be well-balanced between the different atoms.

Dipole moments: Mulliken-Dipole population analysis.

The distribution into equal charges in both orbitals in Mulliken PA, eq. (5), preserves the monopole moment, eq. (6), but, other than that, is arbitrary.⁴⁰ Thus, we turn our attention to the next most important multipole moment of the overlap densities.

The dipole moment of $\rho(\mu, \nu)$ can be written as:

$$\Delta(\mu, \nu) = \int \mathbf{r} \rho(\mu, \nu)(\mathbf{r}) d^3r = (P_{\nu\mu} \mathbf{D}_{\mu\nu} + P_{\mu\nu} \mathbf{D}_{\nu\mu}) + \left(\frac{\mathbf{R}_n + \mathbf{R}_m}{2} \right) Q(\mu, \nu), \quad (8)$$

where the dipole matrix elements $\mathbf{D}_{\mu,\nu}$ are defined w.r.t. the midpoint between atoms m

and n :

$$\mathbf{D}_{\mu\nu} = \int \left(\mathbf{r} - \frac{\mathbf{R}_n + \mathbf{R}_m}{2} \right) \phi_\mu^*(\mathbf{r} - \mathbf{R}_m) \phi_\nu(\mathbf{r} - \mathbf{R}_n) d^3r . \quad (9)$$

The idea is that the charges $q_\mu(\mu, \nu)$ and $q_\nu(\mu, \nu)$ must conserve both the monopole moment, eq. (6), and the dipole moment along the direction from atom m to atom n , \mathbf{u}_{mn} :

$$\Delta(\mu, \nu) \cdot \mathbf{u}_{mn} = (q_\mu(\mu, \nu) \mathbf{R}_m + q_\nu(\mu, \nu) \mathbf{R}_n) \cdot \mathbf{u}_{mn} , \quad (10)$$

with $\mathbf{u}_{mn} = (\mathbf{R}_n - \mathbf{R}_m) / d_{mn}$, where $d_{mn} = |\mathbf{R}_n - \mathbf{R}_m|$ is the distance between atoms m and n . This yields:

$$q_\nu(\mu, \nu) - q_\mu(\mu, \nu) = \frac{2}{d_{mn}} (P_{\nu\mu} D_{\mu\nu}^\parallel - P_{\mu\nu} D_{\nu\mu}^\parallel) , \quad (11)$$

with

$$D_{\mu\nu}^\parallel = \mathbf{D}_{\mu\nu} \cdot \mathbf{u}_{mn} ; \quad (12)$$

if orbitals μ and ν belong to the same atom ($m = n$), then $D_{\nu\mu}^\parallel / d_{mn} = 0$. Intra-atomic dipoles are discussed below. Notice that $D_{\nu\mu}^\parallel = -(D_{\mu\nu}^\parallel)^*$.

Equations (6) and (11) fully determine the charges $q_\mu(\mu, \nu)$, $q_\nu(\mu, \nu)$:

$$q_\mu(\mu, \nu) = \frac{P_{\mu\nu}}{2} (S_{\nu\mu} + C_{\nu\mu}) + \frac{P_{\nu\mu}}{2} (S_{\mu\nu} - C_{\mu\nu}) , \quad (13)$$

$$q_\nu(\mu, \nu) = \frac{P_{\nu\mu}}{2} (S_{\mu\nu} + C_{\mu\nu}) + \frac{P_{\mu\nu}}{2} (S_{\nu\mu} - C_{\nu\mu}) , \quad (14)$$

with

$$C_{\mu\nu} = 2D_{\mu\nu}^\parallel / d_{mn} ; \quad (15)$$

(if $m = n$, $C_{\mu\nu} = 0$). Notice that the matrix \mathbf{C} is anti-hermitian, $C_{\nu\mu} = -C_{\mu\nu}^*$. Adding the contributions from all overlap densities yields the *Mulliken-Dipole* (M-D) PA:

$$q_\mu^{MD} = \frac{1}{2} (\mathbf{PS} + \mathbf{SP})_{\mu\mu} + \frac{1}{2} (\mathbf{PC} - \mathbf{CP})_{\mu\mu} = q_\mu^M + \Delta q_\mu . \quad (16)$$

For real orbitals eq. (16) is simplified to $q_\mu = (\mathbf{PA})_{\mu\mu}$ with $A_{\nu\mu} = (S_{\nu\mu} + C_{\nu\mu})$.

Eq. (16) guarantees the correct description of the monopole *and dipole* moments for each overlap density $\rho(\mu, \nu)$, which are their two most important physical properties. In practice, the M-D PA is straightforward to implement since the matrix elements $D_{\mu\nu}^{\parallel}$ are easily calculated alongside the overlap matrix elements $S_{\mu\nu}$. Thus, it represents an important improvement over the Mulliken PA at practically no computational cost.

As an illustration of eq. (16), Tables 1-4 show the partial atomic charges for the molecules HF, H₂O, NH₃, CH₄, H₂CO (formaldehyde), CH₃OH (methanol) and CH₃NH₂ (methylamine), see Figure 1, as calculated using the Mulliken-Dipole (M-D), Mulliken (M) or Löwdin (L) PA methods. The partial atomic charge (or net atomic charge) in atom m is $\delta_m = Z_m - Q_m$, where Z_m and Q_m are the nuclear and electron charge in atom m . In particular, the M-D partial atomic charges are:

$$\delta_m^{MD} = Z_m - \sum_{\mu \in m} q_\mu^{MD}. \quad (17)$$

In these examples we calculate the electron density $\rho(\mathbf{r})$, eq. (1), by means of a DFT Kohn-Sham calculation, using the LDA exchange-correlation functional and a basis set with *ss** atomic-like orbitals in the H atoms and *spd* atomic-like orbitals in F, O, N and C; these orbitals are obtained from atomic calculations for neutral atoms with the boundary condition that the orbitals vanish at a distance of $R_c = 6$ a.u.^{41,42} Tables 1-4 also show some representative values for the atomic charges, taken from other calculations,^{13,18,19,43-46} using the HIR,⁴ AIM-QT,²⁰ ESP,¹⁰ and CM5¹⁸ methods. Also shown in these Tables are the δ_m^0 atomic charges that will be discussed below; these charges are derived from the M-D charges introducing charge variations that are adjusted to reproduce the molecular dipole moments including the effects of the intra-atomic dipoles.

Let us first compare the Mulliken and M-D results. First thing to notice is that the M-D atomic charges are very different from the Mulliken ones, showing the very important effects

of eq. (11). For example, the Mulliken partial charge for the C atom in the CH₄, H₂CO, CH₃OH and CH₃NH₂ molecules is -1.50, -0.59, -1.13 and -1.06 (in elementary charge units, $+e$), respectively, to be compared with -0.18, -0.02, -0.06 and -0.01 for M-D. In general, the M-D atomic charges are significantly smaller (in absolute value) than the Mulliken charges, and follow the intuitive chemical trends based on the electronegativities of the atoms. Also, notice that the M-D charges are quite similar to the HIR charges, the most significant differences ($\sim 0.16\ e$) appearing for H₂CO, a molecule that presents very large intra-atomic dipoles, see below. A comparison between the different results in Tables 1-4 shows that the largest variations between the different methods appear for the C atoms. In this respect, both the HIR and M-D methods yield small partial charges for the C atoms in the CH₄, H₂CO, CH₃OH and CH₃NH₂ molecules, a result in accord to the chemical intuition. In a recent work¹⁹ different properties related to the atomic charges were analyzed and it was concluded that the HIR method is the more satisfactory one of those tested. Thus, the similarity of the M-D and HIR charges, together with the physical arguments presented above in the derivation of the M-D charges, suggest that the M-D (and HIR) atomic charges are good tools for the conceptual understanding and rationalization of chemical processes.

For practical applications, *e.g.* force fields molecular mechanics simulations or semi-empirical methods, it is important to have a good description of the dipole moments in order to properly model the electrostatic interactions. In many cases intra-atomic dipoles are an important contribution to the dipole moments. We analyze next the relation between the total dipole moment, M-D charges and intra-atomic dipoles. This analysis allows us to introduce charge variations to the M-D atomic charges so that the resulting atomic charges, δ_m^0 , replicate the total dipole moment of the molecule, yielding also a good description of the local charge and dipole moments in the different functional units that make up the molecule.

Total dipole, intra-atomic dipoles and M-D atomic charges.

The total dipole moment of a molecule is the sum of the contributions of the nuclear charges, Z_m , and the electron density:

$$\Delta_T = \Delta_Z + \Delta_E = \sum_m Z_m \mathbf{R}_m - \int \mathbf{r} \rho(\mathbf{r}) d^3r. \quad (18)$$

The term due to the electron density can be written in terms of the density matrix \mathbf{P} as:

$$\Delta_E = - \int \mathbf{r} \rho(\mathbf{r}) d^3r = - \sum_{\mu\nu} P_{\nu\mu} \mathbf{D}_{\mu\nu} - \sum_{\mu\nu} P_{\nu\mu} S_{\mu\nu} \left(\frac{\mathbf{R}_n + \mathbf{R}_m}{2} \right). \quad (19)$$

Since the M-D charges already include the contributions of the dipole moments along the bond directions of all overlap charges, the total dipole moment can be written as (see S.I.):

$$\Delta_T = \sum_m \delta_m^{MD} \mathbf{R}_m + \sum_m \Delta_{I,m}^0 + \delta\Delta, \quad (20)$$

where δ_m^{MD} is the M-D partial charge in atom m , eq. (17), $\Delta_{I,m}^0$ is the intra-atomic dipole in atom m ,

$$\Delta_{I,m}^0 = - \sum_{\mu, \mu' \in m} P_{\mu'\mu} \mathbf{D}_{\mu\mu'}, \quad (21)$$

and $\delta\Delta$ the "residual" dipole associated with the dipole moments perpendicular to the bond directions:

$$\delta\Delta = - \sum_{\mu\nu}^{m \neq n} P_{\nu\mu} (\mathbf{D}_{\mu\nu} - \mathbf{D}_{\mu\nu}^{\parallel}) = - \sum_{\mu\nu}^{m \neq n} P_{\nu\mu} \mathbf{D}_{\mu\nu}^{\perp}; \quad (22)$$

$\mathbf{D}_{\mu\nu}^{\parallel}$ and $\mathbf{D}_{\mu\nu}^{\perp}$ are the components of $\mathbf{D}_{\mu\nu}$ parallel and perpendicular to the bond direction, \mathbf{u}_{mn} . In practice, this contribution can be projected into the intra-atomic dipoles, renormalizing them as follows:

$$\Delta_{I,m} = \Delta_{I,m}^0 - \sum_{\mu \in m} \sum_{\nu}^{n \neq m} \frac{1}{2} (P_{\mu\nu} \mathbf{D}_{\nu\mu}^{\perp} + \mathbf{D}_{\mu\nu}^{\perp} P_{\nu\mu}). \quad (23)$$

This finally yields

$$\Delta_T = \sum_m \delta_m^{MD} \mathbf{R}_m + \sum_m \Delta_{I,m}. \quad (24)$$

In this equation the total dipole is written as a sum of two *atomic* contributions, one associated with the M-D partial atomic charges, δ_m^{MD} , and the other due to the intra-atomic dipoles $\Delta_{I,m}$. A similar expression can be found in the context of HIR PA.^{4,39,44}

In general, the intra-atomic dipoles are an important contribution to the total dipole moment. Tables 5, 6, and Tables S1, S2 in the S.I. show the different contributions to Δ_T , eq. (20), in our test calculations for the HF, H₂O, NH₃, H₂CO, CH₃OH and CH₃NH₂ molecules.⁴⁷ For example, the intra-atomic dipole in the O atom in the H₂O molecule is 0.73 D, out of a total dipole of 1.77 D. A more extreme situation is found for formaldehyde (Table 6), with a very large dipole moment in the C atom (2.37 D), in the opposite direction than the total dipole moment of the molecule; the intra-atomic dipole in the O atom is also large (-1.17 D). As another example, the intra-atomic dipole moment in the C atom in methanol (Table S2) has a magnitude of 1.19 D, with a very different orientation than Δ_T (angle of $\sim 2\pi/3$). These Tables also show how $\delta\Delta$ is incorporated into the intra-atomic dipoles $\Delta_{I,m}$ using eq. (23).

It is clear that, in principle, intra-atomic dipoles should be considered explicitly for an accurate description of the electrostatic interactions in atomistic simulations. In many applications, however, the charge density of the molecule is approximated as a sum of partial atomic charges, δ_m^0 , placed at the atomic positions \mathbf{R}_m (the so called distributed monopole approximation). This is a very attractive approach for *e.g.* force-fields molecular mechanics simulations due to the simplicity of its practical implementation. Different methods have been developed to incorporate the effects of the intra-atomic dipole moments into the partial atomic charges, such as the CMx family (x= 1-5)^{17,18,34-36} or the dipole-preserving approach.³⁷⁻³⁹ These effects are implicitly incorporated in the ESP methods that derive partial atomic charges from the fitting of the electrostatic potential in some region of space.

Eq. (24) offers an alternative approach to derive physically motivated δ_m^0 charges that

replicate the total dipole of the molecule:

$$\sum_m \delta_m^0 \mathbf{R}_m = \mathbf{\Delta}_T, \quad (25)$$

using the idea of locally distributed dipole-preserving charges.³⁸ In this approach, charge variations, dq_k^m , are introduced to include the contribution from the intra-atomic dipoles,

$$\mathbf{\Delta}_{I,m} = \sum_k dq_k^m \mathbf{R}_k, \quad (26)$$

with the condition that

$$\sum_k dq_k^m = 0. \quad (27)$$

Ideally, the electrostatic potential due to $\mathbf{\Delta}_{I,m}$ should be associated to atomic charges close to atom m . Thus, the dq_k^m are minimized in a least square sense, using weighting functions that depend on the interatomic distances, $w_k^m = e^{\lambda|\mathbf{R}_k - \mathbf{R}_m|^2}$, so that dq_k^m are small (in absolute value) and are localized close to atom m (in this work we have used $\lambda = 1 \text{ \AA}^{-2}$).³⁸ The partial δ_m^0 charges are then obtained as

$$\delta_m^0 = \delta_m^{MD} + \sum_k dq_m^k. \quad (28)$$

At variance with the original proposal, we use here δ_m^{MD} as initial charges, and $\mathbf{\Delta}_{I,m}$ for the intra-atomic dipoles in eq. (26). In this way, the total dipole of the molecule $\mathbf{\Delta}_T$, eq. (18), is exactly reproduced by the charges δ_m^0 . The atomic charges δ_m^0 obtained with this approach are shown in the last row in Tables 1-4. These charges are in general quite similar to the ESP and CM5 atomic charges. Interestingly, in the cases where there is a larger difference between ESP and CM5 atomic charges, *e.g.* the C atoms in H_2CO , CH_3OH or CH_3NH_2 , the dipole-preserving M-D charges δ_m^0 present an intermediate value between the CM5 and ESP atomic charges. In similarity to the M-D atomic charges, the dipole-preserving M-D atomic charges δ_m^0 also follow the expected chemical trends. Notice that the δ_m^{MD} atomic

charges already incorporate the local dipole moments (along the bond directions) and the dipole-preserving approach in eqs. (26) and (28) introduces the remaining dipolar effects, see eq. (24), also in a local fashion. Thus, it is to be expected that the atomic charges δ_m^0 in eq. (28) provide a good description of the local partial charges and local dipole moments in the different functional groups that make up the molecule. We conclude that eq. (28) is a very promising approach to derive atomic charges for atomistic simulations.

In summary, we have presented the Mulliken-Dipole PA in which the arbitrary half-and-half partition of the overlap populations is replaced by the physical condition of conservation of the monopole moment and dipole moment along the the bond direction of the overlap densities. Test calculations show that this approach yields very reasonable atomic charges that follow the expected chemical trends and are also quite similar to the Hirshfeld atomic charges. We have also discussed how this approach can be applied to determine atomic charges, δ_m^0 , appropriate for applications in *e.g.* force field molecular mechanics simulations or semiempirical methods. We finally comment that the Mulliken-Dipole atomic charges are conceptually appealing and are very easy to calculate, offering a great compromise between simplicity and accuracy.

Figure 1

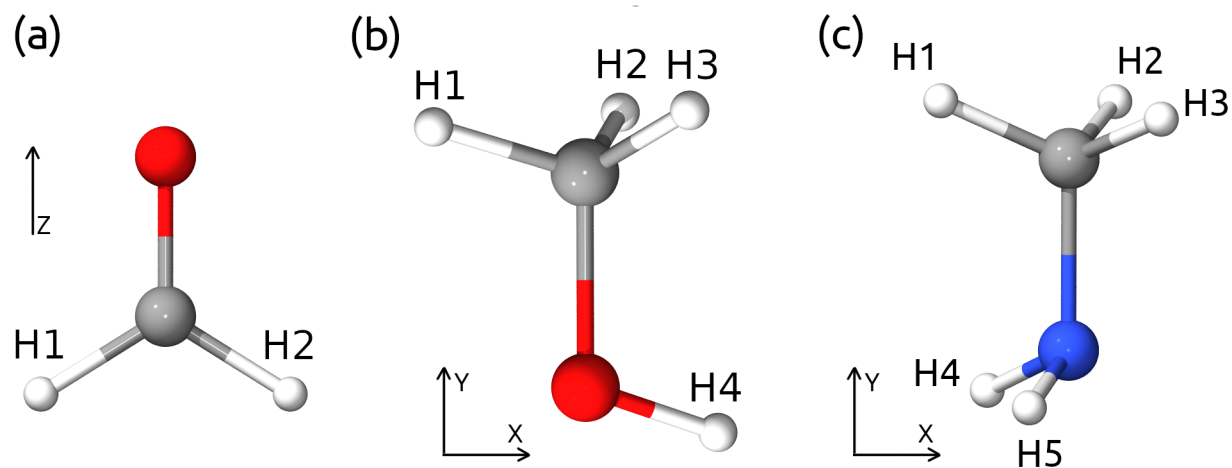


Figure 1: Geometry of the formaldehyde (a), methanol (b) and methylamine (c) molecules. Atoms in white, grey, blue and red correspond to H, C, N, and O, respectively. The different H atoms are indicated.

Tables

Table 1: Mulliken-Dipole (M-D), Mulliken (M), Löwdin (L), Hirshfeld (HIR), Atoms-in-Molecules-Quantum-Theory (AIM-QT), CHELPG (ESP), CM5 and dipole-preserving M-D (δ_m^0) partial atomic charges δ_H (in elementary charge units, $+e$) in the H atoms for the HF, H₂O, NH₃ and CH₄ molecules, see text.

	HF	H ₂ O	NH ₃	CH ₄
M-D	0.29	0.16	0.10	0.04
M	0.57	0.48	0.42	0.37
L	0.41	0.35	0.30	0.25
HIR ¹⁸	0.22	0.16	0.10	0.03
AIM-QT ⁴³	0.78	0.63	0.35	-0.04
ESP ^{13,19}	0.45	0.34	0.29	0.10
CM5 ¹⁸	0.29	0.32	0.28	0.08
δ_H^0	0.40	0.31	0.26	0.04

Table 2: Same as Table 1 for the partial atomic charges δ_m in the different atoms for the formaldehyde molecule, H₂CO, see Figure 1a.

	O	C	H1	H2
M-D	-0.39	-0.02	0.21	0.21
M	-0.27	-0.59	0.43	0.43
L	-0.12	-0.45	0.28	0.28
HIR ¹⁸	-0.23	0.14	0.05	0.05
AIM-QT ⁴⁴	-1.11	1.04	0.04	0.04
ESP (C) ¹⁸	-0.45	0.51	-0.03	-0.03
CM5 ¹⁸	-0.29	0.08	0.11	0.11
δ_m^0	-0.27	0.17	0.05	0.05

Table 3: Same as Table 2 for the partial atomic charges δ_m in the different atoms for the methanol molecule, see Figure 1b.

	H1	H2 / H3	C	H4	O
M-D	0.07	0.05	-0.06	0.26	-0.37
M	0.39	0.37	-1.13	0.51	-0.52
L	0.31	0.29	-0.87	0.41	-0.43
HIR ⁴⁴	0.03	0.03	-0.01	0.16	-0.24
AIM-QT ⁴⁴	0.01	0.01	0.49	0.54	-1.07
ESP ⁴⁴	0.00	0.00	0.23	0.39	-0.61
CM5 ⁴⁵	0.09	0.09	-0.14	0.34	-0.48
δ_m^0	0.09	0.00	0.05	0.40	-0.55

Table 4: Same as Table 2 for the partial atomic charges δ_m in the different atoms for the methylamine (CH_3NH_2) molecule, see Figure 1c.

	C	N	H1	H2 / H3	H4 / H5
M-D	-0.01	-0.29	0.01	0.02	0.13
M	-1.06	-0.76	0.35	0.33	0.40
L	-0.94	-0.69	0.28	0.31	0.36
HIR ⁴⁴	-0.04	-0.22	0.03	0.03	0.10
AIM-QT ⁴⁶	0.62	-1.17	-0.08	-0.05	0.36
ESP ⁴⁶	0.42	-0.94	-0.10	-0.03	0.34
CM5 ⁴⁵	-0.15	-0.68	0.09	0.09	0.28
δ_m^0	0.02	-0.75	0.00	0.05	0.31

Table 5: Molecular dipoles (in Debye) for the HF, H₂O and NH₃ molecules: the total dipole, Δ_T ; the dipole due to the M-D partial atomic charges, $\Delta_Q = \sum_m \delta_m^{MD} \mathbf{R}_m$; the intra-atomic dipoles $\Delta_{I,m}^0$ in the F, O or N atoms; and the residual dipole $\delta\Delta$. Notice that $\Delta_T = \Delta_Q + \Delta_{I,m}^0 + \delta\Delta$.

	HF	H ₂ O	NH ₃
Δ_T	1.75	1.77	1.45
Δ_Q	1.29	0.90	0.55
$\Delta_{I,m}^0$	0.47	0.73	0.61
$\delta\Delta$	0.00	0.13	0.29

Table 6: Cartesian X, Y, Z dipole components (in Debye) for the H₂CO (formaldehyde) molecule in the geometry shown in Figure 1a: Δ_T is the total dipole, eq. (18); $\Delta_Q = \sum_m \delta_m^{MD} \mathbf{R}_m$ is the dipole due to the M-D partial atomic charges; $\Delta_{I,C}^0$ and $\Delta_{I,O}^0$ are the intra-atomic dipoles, eq. (21), for the C and O atoms; $\delta\Delta$ is the residual dipole, eq. (22). $\Delta_{I,C}$, $\Delta_{I,O}$, $\Delta_{I,H1}$ and $\Delta_{I,H2}$ are the renormalized intra-atomic dipoles, eq. (23).

	X	Y	Z
Δ_T	0.00	0.00	-1.80
Δ_Q	0.00	0.00	-3.44
$\Delta_{I,O}^0$	0.00	0.00	-1.17
$\Delta_{I,C}^0$	0.00	0.00	2.37
$\delta\Delta$	0.00	0.00	0.44
$\Delta_{I,O}$	0.00	0.00	-0.99
$\Delta_{I,C}$	0.00	0.00	2.41
$\Delta_{I,H1}$	0.00	0.18	0.11
$\Delta_{I,H2}$	0.00	-0.18	0.11

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Supporting Information: Mulliken-Dipole Population Analysis.

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1 Derivation of equation (20).

We sketch the derivation of eq. (20). First, consider

$$\sum_{\mu} q_{\mu}^{MD} \mathbf{R}_m = \sum_{\mu\nu} \frac{1}{2} P_{\nu\mu} S_{\mu\nu} \mathbf{R}_m + \sum_{\mu\nu} \frac{1}{2} P_{\mu\nu} S_{\nu\mu} \mathbf{R}_m + \sum_{\mu\nu} P_{\mu\nu} \frac{D_{\nu\mu}^{\parallel}}{d_{mn}} \mathbf{R}_m - \sum_{\mu\nu} P_{\nu\mu} \frac{D_{\mu\nu}^{\parallel}}{d_{mn}} \mathbf{R}_m,$$

where we have used eq. (16). Now, interchanging $\mu \leftrightarrow \nu$ (and $m \leftrightarrow n$) in the second and third of these terms:

$$\sum_{\mu} q_{\mu}^{MD} \mathbf{R}_m = \sum_{\mu\nu} P_{\nu\mu} S_{\mu\nu} \left(\frac{\mathbf{R}_m + \mathbf{R}_n}{2} \right) + \sum_{\mu\nu}^{m \neq n} P_{\nu\mu} \frac{D_{\mu\nu}^{\parallel}}{d_{mn}} (\mathbf{R}_n - \mathbf{R}_m),$$

or

$$\sum_{\mu} q_{\mu}^{MD} \mathbf{R}_m = \sum_{\mu\nu} P_{\nu\mu} S_{\mu\nu} \left(\frac{\mathbf{R}_m + \mathbf{R}_n}{2} \right) + \sum_{\mu\nu}^{m \neq n} P_{\nu\mu} \mathbf{D}_{\mu\nu}^{\parallel}$$

(remember that $D_{\mu\nu}^{\parallel}/d_{mn} = 0$ if $m = n$). Also, notice that

$$\sum_{\mu\nu} P_{\nu\mu} \mathbf{D}_{\mu\nu} = \sum_{\mu\nu}^{m \neq n} P_{\nu\mu} \mathbf{D}_{\mu\nu} - \sum_m \Delta_{I,m}^0,$$

(see eq. (21)). Combining these results with eqs. (18) and (19) yields eq. (20).

2 Dipole moment components for CH₃OH and CH₃NH₂.

Table S1: Same as Table 6 for the methanol molecule in the geometry shown in Figure 1b.

	X	Y	Z
Δ_T	1.35	0.53	0.00
Δ_Q	1.05	0.71	0.00
$\Delta_{I,C}^0$	-0.24	-1.17	0.00
$\Delta_{I,O}^0$	0.48	0.80	0.00
$\delta\Delta$	0.06	0.20	0.00
$\Delta_{I,C}$	-0.29	-1.00	0.00
$\Delta_{I,O}$	0.62	0.73	0.00
$\Delta_{I,H1}$	-0.06	-0.02	0.00
$\Delta_{I,H2}$	-0.01	0.02	0.08
$\Delta_{I,H3}$	-0.01	0.02	-0.08
$\Delta_{I,H4}$	0.04	0.09	0.00

Table S2: Same as Table 6 for the methylamine molecule in the geometry shown in Figure 1c.

	X	Y	Z
Δ_T	-1.15	-0.02	0.00
Δ_Q	-0.54	-0.12	0.00
$\Delta_{I,C}^0$	0.25	-0.66	0.00
$\Delta_{I,N}^0$	-0.37	0.54	0.00
$\delta\Delta$	-0.49	0.23	0.00
$\Delta_{I,C}$	0.30	-0.11	0.00
$\Delta_{I,N}$	-0.78	0.10	0.00
$\Delta_{I,H1}$	-0.07	0.02	0.00
$\Delta_{I,H2}$	0.08	0.08	0.06
$\Delta_{I,H3}$	0.08	0.08	-0.06
$\Delta_{I,H4}$	-0.12	-0.03	-0.06
$\Delta_{I,H5}$	-0.12	-0.03	0.06

3 Atomic coordinates for H₂CO, CH₃OH and CH₃NH₂.

Table 1: Atomic coordinates (in Å) for the geometry of the formaldehyde molecule used in this work (from¹).

	X	Y	Z
O	0.0000	0.0000	1.2050
C	0.0000	0.0000	0.0000
H1	0.0000	0.9429	-0.5876
H2	0.0000	-0.9429	-0.5876

Table 2: Atomic coordinates (in Å) for the geometry of the methanol molecule used in this work (from¹).

	X	Y	Z
C	-0.0470	0.6756	0.00
O	-0.0470	-0.7673	0.00
H1	-1.0969	0.9837	0.00
H2	0.4404	1.0870	0.8970
H3	0.4404	1.0870	-0.8970
H4	0.8748	-1.0729	0.00

Table 3: Atomic coordinates (in Å) for the geometry of the methylamine molecule used in this work (from¹).

	X	Y	Z
C	0.0477	0.7016	0.0000
N	0.0477	-0.7505	0.0000
H1	-0.9434	1.1516	0.0000
H2	0.5784	1.0603	0.8726
H3	0.5784	1.0603	-0.8726
H4	-0.4165	-1.1143	-0.8044
H5	-0.4165	-1.1143	0.8044

References

- (1) NIST Computational Chemistry Comparison and Benchmark DataBase. 2019; <http://cccbdb.nist.gov/>.

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