

Extraction of Stewart Atoms from Electron Densities

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Stewart atoms are the unique nuclear-centered spherical functions whose sum best fits a molecular electron density in a least-squares sense. It is difficult, however, to express Stewart atoms in closed form. We therefore introduce new closed-form approximations, Stewart–Slater atoms, and show that these can be found efficiently from molecular multipole moments. Using examples, we argue that the parameters of Stewart–Slater atoms can yield insight into the nature of chemical bonding.

1. Introduction

Because the Schrödinger equation for a molecule makes no reference to the constituent atoms, it is generally acknowledged¹ that it is not possible to derive the atom-in-a-molecule concept from the basic postulates of quantum mechanics. Notwithstanding this, chemists have (and have always had) an overpowering need to rationalize their chemistry in atomic terms. To quote Parr and Yang,² “Chemistry is the science of why particular atoms behave in particular ways, and why also do particular functional groups. Combination does not destroy atomic identity; it only perturbs it slightly, or a little more. An atom here is not the same as an atom there, but it is almost so.” The same authors also point out that “For molecules, at first sight, densities look like superposed atomic densities; on closer inspection, modest (but still quite small in absolute terms) buildups of density are seen in bonding regions.”

Accordingly, over the past few decades, chemists have examined numerous schemes^{2–24} that partition a molecule into its “atomic components”. Every scheme begins with the critical recognition that a partition is possible only after the basic postulates have been augmented by an additional assumption and, although each invokes a different assumption, one must concede in the final analysis that any partition is arbitrary and that its merit can be assessed only in terms of its aesthetic purity, its computational cost, and the usefulness of the resulting model.

According to density functional theory,² all quantities of interest may be deduced from the molecular charge density $\rho(\mathbf{r})$. Of course, the density in a real molecule is a complicated function and it would be helpful to be able to decompose it into simple, atom-centered pieces. This is another significant motivation for seeking a meaningful partition of the density.

Of the various competing definitions of atoms in molecules, Bader’s partition¹⁵ based on the zero-flux surfaces of $\rho(\mathbf{r})$ is undoubtedly one of the most popular. Bader has shown that his atoms possess a wide range of useful properties²¹ and his group have made available a practical computer program,¹¹ PROAIM, that implements their partitioning scheme. The cost of computing Bader atoms, however, is relatively high¹⁶ and the Bader approach has hitherto been restricted to moderate-size molecules.

Analogous comments can be made about the *charge* of an atom in a molecule. For reasons which are closely related to those of the foregoing paragraph, this too defies derivation from quantum mechanical first principles. Indeed, the difficulties here

are probably even greater because, even if it were assumed that one could discern the “atoms” in a molecule, it is still not necessarily clear how one would proceed thence to determine the “atomic charges”. Although it could be argued that the atomic charge should be the integral over all space of the appropriate atom, this is meaningful only if the atom is compactly localized about its nucleus. In an excellent review,¹³ Hall and Smith survey the progress that has been made but conclude that “the goal of defining an atomic charge, within a molecule, which can be calculated readily and used in discussions of molecular bonding and reactivities, has not yet been reached”.

In the present paper, we develop a partitioning scheme based on a remarkable result due to Stewart.^{5,7,8,23} The scheme is conceptually simple and yields chemically useful “atoms” at a modest computational cost. Furthermore, it has interesting connections to the novel Gaussian molecular shape model that has been described recently in the work of Grant and Pickup.²⁴ We have implemented the scheme within the Q-CHEM program²⁵ and all results reported in this paper are in atomic units.

2. Exact Stewart Atoms

Consider an N -atom molecule whose j th nucleus is at \mathbf{A}_j and whose charge density $\rho(\mathbf{r})$ is known. The internuclear distances are $R_{ij} = |\mathbf{A}_i - \mathbf{A}_j|$. Stewart’s assumption is that the j th “atom” in the molecule is a spherically symmetric function σ_j centered on the j th nucleus. The functions σ_j , for which we propose the name “Stewart atoms”, are defined as those whose sum best fits $\rho(\mathbf{r})$ in a least-squares sense.

The Stewart atoms σ_j for a given $\rho(\mathbf{r})$ minimize the residual functional

$$Z(\vartheta) = \int \int [\rho(\mathbf{r}_1) - \sum \sigma_j(r_{1j})] \vartheta(r_{12}) \times [\rho(\mathbf{r}_2) - \sum \sigma_j(r_{2j})] \mathbf{dr}_1 \mathbf{dr}_2 \quad (2.1)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $r_{1j} = |\mathbf{r}_1 - \mathbf{A}_j|$ and the two-electron operator $\vartheta(r_{12})$ determines the fit model. The most important models in practice are $\vartheta(r) \equiv \delta(r)$, r^{-1} or $-r^{+1}$ and these can be shown to fit $\rho(\mathbf{r})$ itself, the electric field due to $\rho(\mathbf{r})$, or the electric potential due to $\rho(\mathbf{r})$, respectively.²⁶ We will call the resulting σ_j density-derived, field-derived, and potential-derived Stewart atoms. Stewart then uses the convolution theorem to rewrite (2.1) in terms of Fourier transforms as

$$Z(\vartheta) = \int F_\vartheta(x) |F_\rho(\mathbf{x}) - \sum F_j(x) e^{i\mathbf{x} \cdot \mathbf{A}_j}|^2 \mathbf{dx} \quad (2.2)$$

Using the calculus of variations to find the $F_j(x)$ that minimize

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$Z(\vartheta)$ yields the linear system

$$\mathbf{J}\mathbf{F} = \mathbf{P} \quad (2.3)$$

where, after integrating over Ω (the angular part of \mathbf{x}), we have

$$J_{ij}(x) = j_0(R_{ij}x) = \sin(R_{ij}x)/R_{ij}x \quad (2.4)$$

$$P_j(x) = \int F_\rho(\mathbf{x}) e^{-i\mathbf{x}\cdot\mathbf{A}_j} d\Omega = \int \rho(\mathbf{r}) j_0(r_jx) d\mathbf{r} \quad (2.5)$$

After solving (2.3) for the $F_j(x)$, the Stewart atoms can be obtained by the back-transformation

$$\sigma_j(r) = \frac{1}{2\pi^2} \int_0^\infty x^2 j_0(rx) F_j(x) dx \quad (2.6)$$

Details of the extraction of Stewart atoms from a diatomic molecule are given below.

Curiously, the fitting operator ϑ disappears during the variation process and, as a result, the σ_j are independent of it. The density-derived, field-derived, and potential-derived Stewart atoms from a given density are therefore all identical, a fact that suggests to us that the Stewart decomposition of the molecular electronic density is a very natural one indeed.

We note that Stewart atoms, unlike Bader atoms, have no boundaries. This is important conceptually for it implies that Stewart atoms overlap and may be regarded as radially perturbed free atoms. Alternatively, Stewart atoms could be interpreted as being “soft” modifications of the traditional “hard-sphere” space-filling models of molecular structure. In either picture, they represent an extension of the “soft Gaussian atoms” recently introduced by Grant and Pickup.²⁴

If desired, the “Stewart charge” $\sigma_j^{(0)}$ can be found by integrating the Stewart atom, *i.e.*

$$\sigma_j^{(0)} = \int \sigma_j(r) d\mathbf{r} = F_j(0) \quad (2.7)$$

and Stewart himself has derived formulas²³ for these in small systems of various symmetries. However, it is important to realize that, whereas the σ_j are optimal in a least-squares sense, the $\sigma_j^{(0)}$ are not. In particular, if a σ_j is poorly localized about its nucleus, the associated $\sigma_j^{(0)}$ is of little physical significance. However, the Stewart charges possess some attractive features. It can be shown,²³ for example, that the Stewart charges (placed at their parent nuclei) exactly reproduce the multipole moments of $\rho(\mathbf{r})$ up to a certain multipole order. This property is very desirable. Indeed, in a recent review,²² Ángyán and Chipot cited it as the most important to be satisfied by a charge distribution model.

To illustrate the extraction of exact Stewart atoms, we consider the case of a diatomic molecule with nucleus 1 at the origin and nucleus 2 at \mathbf{R} . For simplicity, we will assume that $\rho(\mathbf{r})$ is a sum of normalized spherical Gaussians whose centers lie along the bond axis, *i.e.*

$$\rho(\mathbf{r}) = \sum_k U_k \left(\frac{\zeta_k}{\pi} \right)^{3/2} \exp(-\zeta_k |\mathbf{r} - \alpha_k \mathbf{R}|^2) \quad (2.8)$$

$$F_\rho(\mathbf{x}) = \sum_k U_k \exp(i\alpha_k \mathbf{x} \cdot \mathbf{R} - x^2/(4\zeta_k)) \quad (2.9)$$

It follows from (2.3)–(2.5) that the Fourier transforms of the Stewart atoms are given by

$$\begin{bmatrix} F_1(x) \\ F_2(x) \end{bmatrix} = \begin{bmatrix} 1 & j_0(Rx) \\ j_0(Rx) & 1 \end{bmatrix}^{-1} \times \begin{bmatrix} \sum U_{kj_0}(\alpha_k Rx) \exp(-x^2/(4\zeta_k)) \\ \sum U_{kj_0}(\bar{\alpha}_k Rx) \exp(-x^2/(4\zeta_k)) \end{bmatrix} \quad (2.10)$$

where $\bar{\alpha}_k = 1 - \alpha_k$. Substituting $F_1(x)$ into (2.6) then yields the exact Stewart atom

$$\sigma_1(r) = \sum_k \frac{U_k}{2\pi^2} \int_0^\infty \frac{[j_0(\alpha_k Rx) - j_0(Rx)j_0(\bar{\alpha}_k Rx)]}{1 - j_0^2(Rx)} \times x^2 j_0(rx) \exp\left(\frac{-x^2}{4\zeta_k}\right) dx \quad (2.11)$$

By solving (2.10) in the limit of small x , it can be shown that the Stewart charges are

$$\begin{bmatrix} \sigma_1^{(0)} \\ \sigma_2^{(0)} \end{bmatrix} = \begin{bmatrix} F_1(0) \\ F_2(0) \end{bmatrix} = \begin{bmatrix} \sum U_k \bar{\alpha}_k \\ \sum U_k \alpha_k \end{bmatrix} \quad (2.12)$$

Although the Stewart charges successfully reproduce the charge and dipole moment of $\rho(\mathbf{r})$, the fact that they are completely independent of the Gaussian exponents ζ_k is unsatisfactory and supports the remark above that the Stewart charges are physically significant only if the Stewart atoms are well localized about their respective nuclei.

3. Stewart Moments and Stewart–Slater Atoms

Unfortunately, although the foregoing derivation seems to yield exact Stewart atoms, the back-transformation (2.6) yields integrals that are difficult or impossible to handle analytically. We have been unable to solve the integral (2.11), for example, without resorting to quadrature and even our numerical techniques are expensive and unreliable at large r . A less ambitious approach is to seek the low-order radial moments of the σ_j . (We note that Stewart himself has used the second moments to estimate atomic sizes in several molecules.²³) We propose that the σ_j can then be approximately reconstructed from these as described below.

The power series expansions of the elements of \mathbf{J} , \mathbf{F} , and \mathbf{P}

$$J_{ij}(x) = 1 - \frac{R_{ij}^2}{3!} x^2 + \frac{R_{ij}^4}{5!} x^4 - \dots \quad (3.1)$$

$$F_j(x) = \sigma_j^{(0)} - \frac{\sigma_j^{(2)}}{3!} x^2 + \frac{\sigma_j^{(4)}}{5!} x^4 - \dots \quad (3.2)$$

$$P_j(x) = \rho_j^{(0)} - \frac{\rho_j^{(2)}}{3!} x^2 + \frac{\rho_j^{(4)}}{5!} x^4 - \dots \quad (3.3)$$

involve the internuclear distances R_{ij} , the radial moments of the σ_j

$$\sigma_j^{(n)} = \int r^n \sigma_j(r) d\mathbf{r} \quad (3.4)$$

and the radial moments of ρ about the various nuclei

$$\rho_j^{(n)} = \int |\mathbf{r} - \mathbf{A}_j|^n \rho(\mathbf{r}) d\mathbf{r} \quad (3.5)$$

By substituting (3.1)–(3.3) into (2.3) and equating coefficients,

one obtains N coupled matrix equations. If the $\rho_j^{(n)}$ are known (these can be derived from the molecular Cartesian multipole moments), one can use singular value decomposition to solve for the $\sigma_j^{(n)}$. Explicit formulas for the first two Stewart atom moments of various small molecules are given in the Appendix.

Suppose that we have used this approach to find the radial moments of a Stewart atom in a molecule. If *all* of its moments were known, it would be possible to use these to reconstruct the Stewart atom exactly. However, is a useful extrapolation possible if only, say, $\sigma^{(0)}$ and $\sigma^{(2)}$ are known? This appears to be a seriously underdetermined problem since clearly there are an infinite number of different Stewart atoms possessing these two moments.

We have already noted that Stewart's notion of atoms-in-molecules conceives of these as radially distorted free atoms. Guided by this view, and the observation that free atom densities are approximately piecewise exponential,²⁷ we propose that a Stewart atom may be modeled satisfactorily by a linear combination of exponentials. Specifically, first-, second-, and third-row Stewart atoms will be approximated by

$$\sigma_{\text{H-He}}(r) \approx Q \left(\frac{\alpha^3}{\pi} \right) e^{-2\alpha r} \quad (3.6)$$

$$\sigma_{\text{Li-Ne}}(r) \approx 2 \left(\frac{c_1^3}{\pi} \right) e^{-2c_1 r} + Q \left(\frac{\alpha^5}{96\pi} \right) r^2 e^{-\alpha r} \quad (3.7)$$

$$\sigma_{\text{Na-Ar}}(r) \approx 2 \left(\frac{c_1^3}{\pi} \right) e^{-2c_1 r} + 8 \left(\frac{c_2^5}{96\pi} \right) r^2 e^{-c_2 r} + Q \left(\frac{2\alpha^7}{98415\pi} \right) r^4 e^{-2\alpha r/3} \quad (3.8)$$

where the c_i are standard Slater exponents²⁸ and the amplitude Q and valence exponent α are chosen to reproduce $\sigma^{(0)}$ and $\sigma^{(2)}$. It is easy to show that the parameters in (3.6) are given by

$$Q = \sigma^{(0)} \quad (3.9)$$

$$\alpha = \sqrt{\frac{3\sigma^{(0)}}{\sigma^{(2)}}} \quad (3.10)$$

while those in (3.7) are

$$Q = \sigma^{(0)} - 2 \quad (3.11)$$

$$\alpha = \sqrt{\frac{30Q}{\sigma^{(2)} - 6c_1^{-2}}} \quad (3.12)$$

and those in (3.8) are

$$Q = \sigma^{(0)} - 10 \quad (3.13)$$

$$\alpha = \sqrt{\frac{126Q}{\sigma^{(2)} - 6c_1^{-2} - 240c_2^{-2}}} \quad (3.14)$$

We will refer to the functions (3.6)–(3.8) as Stewart–Slater atoms. These “atoms” have a standard Slater core but an outer region with, in general, a nonstandard valence exponent α and a nonintegral number Q of valence electrons.

We note in passing that, when higher Stewart moments are available, one can construct “double-split-valence” Stewart–Slater atoms. These are analogous to (3.6)–(3.8) but have *two* valence amplitudes and *two* valence exponents chosen to

TABLE 1: Second Radial Moments and Stewart Exponents in Atoms and Their Ions^a

atom	cation		neutral		anion	
	$\sigma^{(2)}$	α	$\sigma^{(2)}$	α	$\sigma^{(2)}$	α
H	0.00000		3.00631	1.00	16.6142	0.60
He	0.75340	2.00	2.37633	1.59	16.4265	
Li	0.89167		18.6594	1.30	85.5732	0.84
Be	7.28480	2.09	17.3306	1.88	63.5252	1.19
B	9.22676	2.59	15.8156	2.41	36.1276	1.83
C	8.11862	3.37	13.8180	2.97	25.7429	2.42
N	7.81729	3.95	12.1329	3.54	23.0608	2.80
O	7.40477	4.53	11.2578	4.02	18.3238	3.39
F	7.16381	5.04	10.2806	4.54	15.5376	3.94
Ne	6.82876	5.57	9.39476	5.07	18.5979	
Na	6.40361		27.2167	2.39	100.343	1.63
Mg	14.0205	3.54	29.6572	3.13	106.238	1.92
Al	17.2968	4.21	33.1742	3.55	66.8512	2.81
Si	20.0798	4.64	32.1561	4.12	53.6081	3.51
P	20.9607	5.16	30.5152	4.71	48.8470	4.02
S	20.8119	5.75	29.3139	5.24	42.9056	4.63
Cl	20.7686	6.26	27.7987	5.79	38.1730	5.24
Ar	20.2193	6.82	26.0643	6.38	48.7676	

^a From UHF/6-311++G(*d,p*) electron densities.

reproduce $\sigma^{(0)}$, $\sigma^{(2)}$, $\sigma^{(4)}$, and $\sigma^{(6)}$. We have not examined these more accurate approximate Stewart atoms in the present paper.

The Stewart–Slater decomposition provides a convenient, semiquantitative route to the electrostatic potential in and around a molecule. This is of central importance for semiclassical modeling in many different contexts. The potentials of Slater-type density functions are given by the simple expressions

$$V \left[\left(\frac{\beta^3}{8\pi} \right) e^{-\beta r} \right] = \frac{1}{r} - \frac{e^{-z}}{r} \left(1 + \frac{z}{2} \right) \quad (3.15)$$

$$V \left[\left(\frac{\beta^5}{96\pi} \right) r^2 e^{-\beta r} \right] = \frac{1}{r} - \frac{e^{-z}}{r} \left(1 + \frac{3z}{4} + \frac{z^2}{4} + \frac{z^3}{24} \right) \quad (3.16)$$

$$V \left[\left(\frac{\beta^7}{2880\pi} \right) r^4 e^{-\beta r} \right] = \frac{1}{r} - \frac{e^{-z}}{r} \left(1 + \frac{5z}{6} + \frac{z^2}{3} + \frac{z^3}{12} + \frac{z^4}{72} + \frac{z^5}{720} \right) \quad (3.17)$$

where $z = \beta r$. We will report results using this approach elsewhere.

4. Results and Discussion

We do not seek in this paper to present an exhaustive numerical study of Stewart atoms. Rather, we have selected a sample of mainly organic molecules and studied these carefully in an attempt to learn something about the typical behavior of Stewart and Stewart–Slater atoms. All of the data discussed below are based on unrestricted Hartree–Fock (UHF) densities. This level suffices for our present purposes for it is well-known that the effects of correlation on molecular densities are generally quite small. Moreover, the basis set that we have employed, 6-311++G(*d,p*), is fairly large and well balanced and yields results quite close to the HF limit. All calculations were performed using the Q-CHEM program²⁵ on an IBM 43P workstation.

To begin, we calculated the first two radial moments of the density of the first 18 atoms and their cations and anions. These are listed in Table 1 with the Stewart exponent α of the corresponding Stewart–Slater atoms. The exponents, which turn out to be slightly smaller than the standard valence Slater values,²⁸ are a useful reference set against which to compare the exponents of Stewart atoms in molecules.

TABLE 2: Radial Moments about Nuclei in Hydrides^a

molecule		$\rho^{(0)}$	$\rho^{(2)}$	$\rho^{(4)}$	$\rho^{(6)}$	$\rho^{(8)}$
H ₂	H	2.00000	6.12247	40.7147	473.765	8 395.74
LiH	Li	4.00000	26.9052	510.025	15763.8	1 127 890
	H	4.00000	31.1758	378.068	7770.90	557 740
BeH ₂	Be	6.00000	31.6082	383.503	7088.32	191 800
	H	6.00000	69.6748	1579.54	50563.9	2 032 730
BH ₃	B	8.00000	34.5908	330.535	4895.63	105 269
	H	8.00000	75.1215	1183.36	25923.1	737 344
CH ₄	C	10.0000	35.7759	285.267	3712.88	78 381.9
	H	10.0000	78.1777	970.711	16981.1	406 530
NH ₃	N	10.0000	26.9878	185.483	2330.11	52 842.1
	H	10.0000	61.7379	613.345	9163.29	206 468
OH ₂	O	10.0000	19.7687	108.946	1114.69	20 275.5
	H	10.0000	50.1919	393.869	4683.02	83 965.1
FH	F	10.0000	13.9224	57.8241	454.895	6 265.01
	H	10.0000	41.7578	255.447	2288.34	30 103.5
NaH	Na	12.0000	40.3036	826.126	29411.8	2 235 450
	H	12.0000	151.195	2283.85	42767.7	1 818 130
MgH ₂	Mg	14.0000	54.6537	896.200	22328.5	790 150
	H	14.0000	202.817	5278.10	223720	12 716 600
AlH ₃	Al	16.0000	63.7955	887.964	18723.3	594 013
	H	16.0000	208.062	4335.69	133852	5 561 330
SiH ₄	Si	18.0000	69.0237	824.608	14745.7	376 062
	H	18.0000	210.367	3741.17	94638.7	3 169 720
PH ₃	P	18.0000	56.5346	603.288	10224.1	258 967
	H	18.0000	174.048	2476.11	51872.2	1 551 750
SH ₂	S	18.0000	44.6225	403.613	6156.84	145 233
	H	18.0000	149.756	1804.93	32402.0	853 419
ClH	Cl	18.0000	34.4393	252.336	3245.95	68 254.7
	H	18.0000	130.790	1334.45	20009.5	441 817

^a From HF/6-311++G(d,p)//MP2/6-31G(d) electron densities.

The radial moments $\rho^{(n)}$ of the first-row and second-row hydrides are listed in Table 2. We have then used these, and formulas A.8–A.13, to calculate $\sigma^{(0)}$ and $\sigma^{(2)}$ for each of the Stewart atoms in these molecules. These moments, along with Stewart charges and exponents from (3.9)–(3.14) and the Mulliken charges, are given in Table 3. Using a singular value decomposition to solve for the $\sigma^{(n)}$, we have also obtained the Stewart moments, charges, and exponents and Mulliken charges of a number of other molecules and these are listed in Table 4.

The Stewart charges in Table 3 yield simple but important insights into the nature of the bonding in the molecules considered. Moving along a row of the Periodic Table from the alkali hydrides to the hydrogen halides, the H atom charge changes from negative (−0.78 in LiH) to positive (+0.47 in HF), as one would expect. Both the Stewart and Mulliken charges on H are shown in Figure 1 and, while the two schemes show similar gross trends, it is clear that they differ substantially in detail. Apart from SiH₄ and PH₃, the Stewart charges are consistently larger than the Mulliken counterparts. The hydride with the least polar bonds is PH₃ (Stewart) or H₂S (Mulliken): standard Pauling electronegativity values²⁹ support the Stewart choice.

Because the Stewart exponent α is related to the radial extent of the Stewart atom, it may be used to deduce the effects of bonding on the sizes of atoms. For example, the increase in α from 1.00 in the free H atom to 1.20 in H₂ illustrates the contraction that accompanies bond formation, a phenomenon that has been recognized since the early days of molecular quantum mechanics³⁰ and which has been cited³¹ as the driving force for bonding in the H₂⁺ molecule. We observe an analogous effect in the isoelectronic species Li₂ but, in contrast, no contraction is observed in N₂ and, indeed, a very slight expansion is found in F₂.

The heavy atom exponents in the metal hydrides are much greater than in the free atoms suggesting compact quasi-cations. Conversely, the H exponents in LiH and NaH are smaller than

TABLE 3: Stewart Moments, Stewart Parameters, and Mulliken Charges in Hydrides^a

molecule		Stewart moments		Stewart parameters		Mulliken charge
		$\sigma^{(0)}$	$\sigma^{(2)}$	charge	α	
H ₂	H	1.000 00	2.090 95	0.000	1.20	0.000
LiH	Li	2.222 43	2.218 05	+0.778	2.19	+0.420
	H	1.777 57	7.623 03	−0.778	0.84	−0.420
BeH ₂	Be	3.334 85	7.890 79	+0.665	2.32	+0.333
	H	1.332 58	3.404 26	−0.333	1.08	−0.167
BH ₃	B	4.299 68	6.765 54	+0.700	3.26	+0.211
	H	1.233 44	3.026 06	−0.233	1.11	−0.070
CH ₄	C	6.578 28	14.321 5	−0.578	3.12	−0.469
	H	0.855 43	1.736 44	+0.145	1.22	+0.117
NH ₃	N	7.984 86	15.557 0	−0.985	3.41	−0.675
	H	0.671 71	1.330 30	+0.328	1.23	+0.225
OH ₂	O	8.788 53	13.647 0	−0.789	3.88	−0.512
	H	0.605 73	1.031 57	+0.394	1.33	+0.256
FH	F	9.468 65	11.476 3	−0.469	4.43	−0.308
	H	0.531 35	0.791 21	+0.469	1.42	+0.308
NaH	Na	10.223 2	8.509 73	+0.777	2.90	+0.503
	H	1.776 76	8.467 23	−0.777	0.79	−0.503
MgH ₂	Mg	11.034 0	14.030 1	+0.966	3.59	+0.603
	H	1.483 01	4.617 03	−0.483	0.98	−0.301
AlH ₃	Al	11.765 3	12.855 2	+1.235	4.78	+0.863
	H	1.411 55	4.252 59	−0.412	1.00	−0.288
SiH ₄	Si	13.421 9	21.887 3	+0.578	4.72	+0.799
	H	1.1445 3	2.796 82	−0.145	1.11	−0.200
PH ₃	P	15.223 8	30.842 7	−0.224	4.78	+0.244
	H	0.925 39	1.952 64	+0.075	1.19	−0.081
SH ₂	S	16.310 9	30.019 8	−0.311	5.30	−0.064
	H	0.844 55	1.890 27	+0.155	1.16	+0.032
ClH	Cl	17.234 2	28.270 3	−0.234	5.83	−0.133
	H	0.765 80	1.688 59	+0.234	1.17	+0.133

^a From HF/6-311++G(d,p)//MP2/6-31G(d) electron densities.

unity and attest to the diffuseness of the quasi-anionic hydride moiety. In general, the H exponents in the hydrides studied can be rationalized by two propositions: (a) when the atom becomes bonded, it tends to contract; (b) if the atom becomes positively (negatively) charged by bonding, it tends to contract

TABLE 4: Stewart Moments, Stewart Parameters, and Mulliken Charges in Other Molecules^a

molecule		Stewart moments		Stewart parameters		Mulliken charge
		$\sigma^{(0)}$	$\sigma^{(2)}$	charge	α	
Li ₂	Li	3.000 00	13.3636	0.000	1.55	0.000
N ₂	N	7.000 00	12.0911	0.000	3.54	0.000
F ₂	F	9.000 00	10.4340	0.000	4.50	0.000
LiF	Li	2.121 92	1.31726	+0.878	2.72	+0.689
	F	9.878 08	13.5989	-0.878	4.18	-0.689
CO	C	5.957 32	13.7527	+0.043	2.96	+0.090
	O	8.042 68	10.6812	-0.043	4.14	-0.090
CO ₂	C	5.104 44	8.68989	+0.896	3.31	+0.646
	O	8.447 78	12.0374	-0.448	4.03	-0.323
CH ₃ F	C	5.874 24	11.6252	+0.126	3.19	-0.137
	H	0.945 11	1.59983	+0.055	1.33	+0.124
	F	9.285 03	11.2852	-0.285	4.42	-0.236
CH ₂ F ₂	C	5.532 84	11.0608	+0.467	3.12	+0.160
	H	0.959 02	1.33884	+0.041	1.47	+0.137
	F	9.272 59	10.8984	-0.273	4.49	-0.217
CHF ₃	C	5.338 75	11.3414	+0.661	3.00	+0.422
	H	0.938 66	0.99340	+0.061	1.68	+0.192
	F	9.240 14	10.5379	-0.240	4.56	-0.205
C ₂ H ₂	C	6.314 32	14.7159	-0.314	2.98	-0.215
	H	0.685 68	0.84678	+0.314	1.56	+0.215
C ₂ H ₄	C	6.397 44	15.7684	-0.397	2.91	-0.221
	H	0.801 28	1.02269	+0.199	1.53	+0.110
C ₂ H ₆	C	5.694 73	4.76645	+0.305	4.92	-0.341
	H	1.101 76	3.41317	-0.102	0.98	+0.114
C ₃ H ₃ ⁺	C	5.88740	10.2853	+0.113	3.40	+0.033
	H	0.779 27	1.41283	+0.221	1.29	+0.300
C ₆ H ₆	C	6.154 05	14.3378	-0.154	2.97	-0.190
	H	0.8459 5	0.94835	+0.154	1.64	+0.190

^a From HF/6-311++G(d,p)/HF/6-31G(d) electron densities.

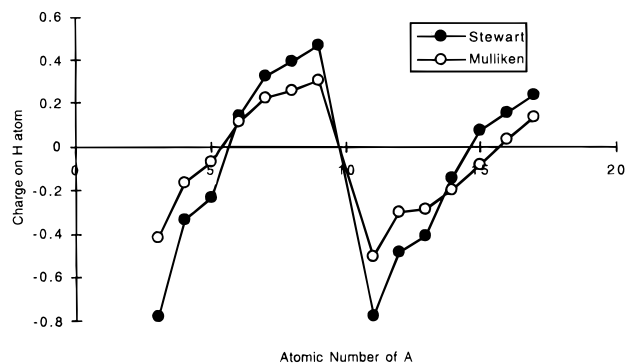


Figure 1. H atom charge in AH_n (values from Table 3).

(expand). The net effect of bonding on the atom's size is the sum of these two, possibly opposing, effects and we note in passing that AlH₃ appears to be a system in which almost perfect cancellation occurs.

The LiF molecule exemplifies highly ionic bonding and is commonly represented Li⁺F⁻ but its Mulliken charges (± 0.69) imply much less polarity than do the Stewart values (± 0.88). The latter, it should be noted, reproduce the dipole moment of the electron density exactly. The Li exponent is more than double that of the free Li atom and, indeed, the $\sigma_{\text{Li}}^{(2)}$ value in Table 4 is not much greater than that of the Li⁺ cation. Likewise, the F exponent is closer to that of the F⁻ anion than the free F atom.

The dipole moment of the CO molecule is small and its direction (the O atom is positive) is predicted incorrectly by Hartree-Fock theory but this is of no consequence for our purposes. We find that the Mulliken charges are twice as large as the Stewart ones but that both are very small. The C and O Stewart atoms are both similar in size to free atoms. The Stewart analysis of the CO₂ molecule, however, is strikingly

different yielding highly charged atoms. Indeed, the charge and exponent of the Stewart C atom are very close to those of a C⁺ cation.

Stewart has previously calculated²³ the charges of the fluoromethanes CH_nF_{4-n} and we have included results for CH₃F, CH₂F₂, and CHF₃ in Table 4. The charge distribution in these systems is of interest and we find that the Stewart and Mulliken analyses afford rather different descriptions. While agreeing that the F atoms bear significant negative charges that diminish slightly as the degree of substitution increases, they disagree in their allocation of the resulting positive charge. More specifically, while the Stewart analysis allots almost no charge at all to the H atoms and leaves the C atom to shoulder this burden alone, the Mulliken analysis is more equitable and uses the H atoms to reduce the C charge by roughly 1/4. In CH₃F, however, the Mulliken scheme leads to the counterintuitive proposition that the C atom is *negatively* charged.

Table 4 concludes with systems containing a variety of C-C bond types: single, double, triple, and aromatic. The charges on the C atoms are surprisingly variable considering that these molecules are all hydrocarbons. The Mulliken and Stewart schemes concur that the alkene, alkyne, and benzene C atoms bear negative charges but the Stewart charges are larger than the Mulliken ones in C₂H₂ and C₂H₄ and smaller in C₆H₆. The C atoms in all three compounds are found by Stewart analysis to be similar in size to free C atoms whereas the H atoms, which bear positive charges, are found to be much smaller than their free counterparts. The simplest aromatic molecule is the cyclopropenium cation C₃H₃⁺ and it is intriguing to find that, whereas Mulliken analysis puts almost all of the excess charge on the H atoms, Stewart analysis places a third of it on the ring and yields C atoms that are only as large as C⁺ cations.

The Stewart results for C₂H₆ contain a cautionary message. Because the C atoms in this molecule are "buried" within a shell of H atoms, they are relatively unimportant for modeling the molecular density. Stewart analysis therefore allots relatively little density to them and, as a consequence, they are positively charged. Moreover, the resulting Stewart exponent is anomalously large indicating, at first glance, an extremely compact atom. The true explanation, however, for the surprisingly small second moment of the C atom is that $\sigma_{\text{C}}(r)$ is not strictly positive. This is confirmed by its *fourth* moment which we find to be negative. We conjecture that it may not be uncommon for the Stewart atoms of "buried" nuclei to contain nodes.

The last stage in this preliminary investigation is to examine the effect of basis set on Stewart atoms. It is well-known that Mulliken analysis is very sensitive to the basis used and that, in order to obtain meaningful charges, it is important that the set used be "well balanced". To study the sensitivity of the Stewart charges and exponents, we arbitrarily selected the CH₃F molecule and performed a Stewart analysis on its Hartree-Fock density determined with a range of basis sets from STO-3G to 6-311++G(3df,3pd). The results are summarized in Table 5 and it is clear from these that the charges are strongly basis set dependent but that the exponents are much less so. The instability of the Stewart charges is a direct reflection of the instability of the molecular dipole moment with respect to basis set improvements.

5. Concluding Remarks

We have shown that Stewart's scheme for partitioning molecular electron densities yields "atoms" that are intuitively plausible and chemically useful. By augmenting his approach with the additional approximation that the valence part of a

TABLE 5: Dipole Moment and Stewart Parameters in the CH₃F Molecule^a

basis set	dipole moment	C parameters		H parameters		F parameters	
		charge	α	charge	α	charge	α
STO-3G	1.1373	-0.028	3.14	+0.054	1.39	-0.131	5.01
3-21G	2.1948	+0.202	3.09	+0.036	1.40	-0.306	4.61
6-31G	2.4322	+0.295	3.17	+0.021	1.37	-0.354	4.48
6-311G	2.4400	+0.276	3.16	+0.027	1.39	-0.351	4.45
6-31G(d)	1.9894	+0.082	3.14	+0.059	1.36	-0.257	4.55
6-311G(d)	2.0912	+0.093	3.13	+0.061	1.38	-0.271	4.50
6-311G(d,p)	2.0737	+0.093	3.15	+0.060	1.37	-0.269	4.50
6-311++G(d,p)	2.1530	+0.121	3.17	+0.056	1.34	-0.284	4.42
6-311++G(d,p)	2.1537	+0.126	3.19	+0.055	1.33	-0.285	4.42
6-311++G(2d,2p)	2.0318	+0.045	3.16	+0.071	1.33	-0.254	4.44
6-311++G(3d,3p)	1.9831	+0.016	3.14	+0.077	1.33	-0.242	4.45
6-311++G(3df,3pd)	1.9800	+0.034	3.15	+0.072	1.33	-0.245	4.45

^a From Hartree–Fock densities at the HF/6-31G(d) geometry.

Stewart atom is a Slater exponential, we have demonstrated that the calculations can be automated and run as an inexpensive population analysis tool in a quantum chemistry package. We propose that a sum of Stewart–Slater atoms may constitute a useful and computationally efficient approximate molecular density for use in a variety of contexts. We will report further on such applications in a subsequent paper.

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Appendix: Stewart Moments in Various Molecules

Applying the theory of section 3 to a diatomic AB yields the coupled matrix equation

$$\begin{bmatrix} \mathbf{1} & \mathbf{T} \\ \mathbf{T} & \mathbf{1} \end{bmatrix} \begin{bmatrix} \sigma_A \\ \sigma_B \end{bmatrix} = \begin{bmatrix} \rho_A \\ \rho_B \end{bmatrix} \quad (\text{A.1})$$

$$\mathbf{T} = \begin{bmatrix} 1 & & & & & & & & \\ R^2 & 1 & & & & & & & \\ R^4 & 10/3R^2 & 1 & & & & & & \\ R^6 & 7R^4 & 7R^2 & 1 & & & & & \\ R^8 & 12R^6 & 12/5R^4 & 12R^2 & 1 & & & & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & & & \end{bmatrix} \quad (\text{A.2})$$

In the case of a homonuclear diatomic A₂, symmetry reduces (A.1) to

$$(\mathbf{1} + \mathbf{T})\sigma = \rho \quad (\text{A.3})$$

and the invertibility of the $(\mathbf{1} + \mathbf{T})$ matrix quickly yields

$$\begin{bmatrix} \sigma_A^{(0)} \\ \sigma_A^{(2)} \\ \sigma_A^{(4)} \\ \sigma_A^{(6)} \\ \sigma_A^{(8)} \\ \sigma_A^{(10)} \\ \vdots \end{bmatrix} = \begin{bmatrix} +1/2 & & & & & & \\ -1/4R^2 & +1/2 & & & & & \\ +1/6R^4 & -5/6R^2 & +1/2 & & & & \\ +1/24R^6 & +7/6R^4 & -7/4R^2 & +1/2 & & & \\ -11/10R^8 & +1/2R^6 & +21/5R^4 & -3R^2 & +1/2 & & \\ +21/4R^{10} & -121/6R^8 & +11/4R^6 & +11R^4 & -55/12R^2 & +1/2 & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \rho_A^{(0)} \\ \rho_A^{(2)} \\ \rho_A^{(4)} \\ \rho_A^{(6)} \\ \rho_A^{(8)} \\ \rho_A^{(10)} \\ \vdots \end{bmatrix} \quad (\text{A.4})$$

In the case of a general heteronuclear diatomic, (A.1) has the formal solution

$$\begin{bmatrix} \sigma_A \\ \sigma_B \end{bmatrix} = (\mathbf{1} - \mathbf{T}^2)^{-1} \begin{bmatrix} \mathbf{1} & -\mathbf{T} \\ -\mathbf{T} & \mathbf{1} \end{bmatrix} \begin{bmatrix} \rho_A \\ \rho_B \end{bmatrix} \quad (\text{A.5})$$

but this expression seems problematic because $(\mathbf{1} - \mathbf{T}^2)$ does not possess a well-defined inverse. Analogous problems are observed for any polyatomic and reflect the fact that the elements of ρ_1 and ρ_2 are not all independent. In particular, we have $\rho_A^{(0)} = \rho_B^{(0)}$. To avoid the singularity in $(\mathbf{1} - \mathbf{T}^2)$, however, one can employ a pseudoinverse such as

$$(\mathbf{1} - \mathbf{T}^2)^{-1} = \begin{bmatrix} 0 & -1/2R^{-2} & & & & & \\ 0 & +2/5 & -3/20R^{-2} & & & & \\ 0 & -52/105R^2 & +2/5 & -1/14R^{-2} & & & \\ 0 & +16/25R^4 & -26/25R^2 & +2/5 & -1/24R^{-2} & & \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \end{bmatrix} \quad (\text{A.6})$$

Substitution of (A.2) and (A.6) into (A.5) yields

$$\begin{bmatrix} \sigma_A^{(0)} \\ \sigma_A^{(2)} \\ \sigma_A^{(4)} \\ \sigma_A^{(6)} \\ \vdots \end{bmatrix} = \begin{bmatrix} +1/2 \\ -1/4R^2 \\ +1/6R^4 \\ +1/24R^6 \\ \vdots \end{bmatrix} \rho^{(0)} + \begin{bmatrix} -1/2R^{-2} & & & & \\ +4/10 & -3/20R^{-2} & & & \\ -104/210R^2 & +4/10 & -1/14R^{-2} & & \\ +96/150R^4 & -104/100R^2 & +4/10 & -1/24R^{-2} & \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \rho_A^{(2)} \\ \rho_A^{(4)} \\ \rho_A^{(6)} \\ \rho_A^{(8)} \\ \vdots \end{bmatrix} + \begin{bmatrix} +1/2R^{-2} & & & & \\ +1/10 & +3/20R^{-2} & & & \\ -71/210R^2 & +1/10 & +1/14R^{-2} & & \\ +79/150R^4 & -71/100R^2 & +1/10 & +1/24R^{-2} & \\ \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} \rho_B^{(2)} \\ \rho_B^{(4)} \\ \rho_B^{(6)} \\ \rho_B^{(8)} \\ \vdots \end{bmatrix} \quad (\text{A.7})$$

In this way, we have obtained formulas for the following stoichiometries and symmetries:

AB (point group = $C_{\infty v}$)

$$\sigma_A^{(0)} = \frac{\rho^{(0)}}{2} - \frac{\rho_A^{(2)} - \rho_B^{(2)}}{2R^2} \quad (\text{A.8})$$

$$\sigma_A^{(2)} = -\frac{R^2\rho^{(0)}}{4} + \frac{4\rho_A^{(2)} + \rho_B^{(2)}}{10} - \frac{3\rho_A^{(4)} - 3\rho_B^{(4)}}{20R^2}$$

AB₂ (point group = $D_{\infty h}$)

$$\sigma_A^{(0)} = \frac{11\rho^{(0)}}{8} + \frac{5\rho_A^{(2)}}{4R^2} + \frac{3\rho_A^{(4)} - 3\rho_B^{(4)}}{8R^4}$$

$$\sigma_B^{(0)} = -\frac{3\rho^{(0)}}{16} - \frac{5\rho_A^{(2)}}{8R^2} - \frac{3\rho_A^{(4)} - 3\rho_B^{(4)}}{16R^4}$$

$$\sigma_A^{(2)} = \frac{3R^2\rho^{(0)}}{28} + \frac{87\rho_A^{(2)}}{56} + \frac{24\rho_A^{(4)} - 3\rho_B^{(4)}}{56R^2} + \frac{3\rho_A^{(6)} - 3\rho_B^{(6)}}{56R^4}$$

$$\sigma_B^{(2)} = \frac{15R^2\rho^{(0)}}{112} + \frac{39\rho_A^{(2)}}{112} - \frac{3\rho_A^{(4)} + 18\rho_B^{(4)}}{112R^2} - \frac{3\rho_A^{(6)} - 3\rho_B^{(6)}}{112R^4} \quad (\text{A.9})$$

AB₃ (point group = D_{3h})

$$\sigma_A^{(0)} = \frac{5\rho^{(0)}}{2} + \frac{5\rho_A^{(2)}}{R^2} + \frac{3\rho_A^{(4)} - 3\rho_B^{(4)}}{2R^4}$$

$$\sigma_B^{(0)} = -\frac{\rho^{(0)}}{2} - \frac{5\rho_A^{(2)}}{3R^2} - \frac{\rho_A^{(4)} - \rho_B^{(4)}}{2R^4}$$

$$\sigma_A^{(2)} = \frac{15R^2\rho^{(0)}}{14} + \frac{75\rho_A^{(2)}}{14} + \frac{33\rho_A^{(4)} - 12\rho_B^{(4)}}{14R^2} + \frac{3\rho_A^{(6)} - 3\rho_B^{(6)}}{14R^4}$$

$$\sigma_B^{(2)} = \frac{R^2\rho^{(0)}}{7} + \frac{3\rho_A^{(2)}}{14} - \frac{4\rho_A^{(4)} + 3\rho_B^{(4)}}{14R^2} - \frac{\rho_A^{(6)} - \rho_B^{(6)}}{14R^4} \quad (\text{A.10})$$

AB₄ (point group = T_d)

$$\sigma_A^{(0)} = \frac{7\rho^{(0)}}{16} - \frac{63\rho_A^{(2)}}{16R^2} - \frac{63\rho_A^{(4)}}{16R^4} - \frac{9\rho_A^{(6)} - 9\rho_B^{(6)}}{16R^6}$$

$$\sigma_B^{(0)} = \frac{9\rho^{(0)}}{64} + \frac{63\rho_A^{(2)}}{64R^2} + \frac{63\rho_A^{(4)}}{64R^4} + \frac{9\rho_A^{(6)} - 9\rho_B^{(6)}}{64R^6}$$

$$\sigma_A^{(2)} = -\frac{83R^2\rho^{(0)}}{320} - \frac{21\rho_A^{(2)}}{20} - \frac{427\rho_A^{(4)}}{160R^2} - \frac{62\rho_A^{(6)} - 17\rho_B^{(6)}}{80R^4} - \frac{3\rho_A^{(8)} - 3\rho_B^{(8)}}{64R^6}$$

$$\sigma_B^{(2)} = -\frac{97R^2\rho^{(0)}}{1280} - \frac{151\rho_A^{(2)}}{320} - \frac{203\rho_A^{(4)}}{640R^2} + \frac{17\rho_A^{(6)} + 28\rho_B^{(6)}}{320R^4} + \frac{3\rho_A^{(8)} - 3\rho_B^{(8)}}{256R^6} \quad (\text{A.11})$$

AB₂ (point group = C_{2v})

$$\sigma_A^{(0)} = \frac{(2R_{AB}^2 - R_{BB}^2)\rho^{(0)} - 2\rho_A^{(2)} + 2\rho_B^{(2)}}{4R_{AB}^2 - R_{BB}^2}$$

$$\sigma_B^{(0)} = \frac{R_{AB}^2\rho^{(0)} + \rho_A^{(2)} - \rho_B^{(2)}}{4R_{AB}^2 - R_{BB}^2}$$

$$\sigma_A^{(2)} = [(3R_{BB}^4 - 32R_{AB}^4)\sigma_A^{(0)} + (6R_{AB}^4 - 3R_{BB}^4)\rho^{(0)} + 20R_{AB}^2\rho_B^{(2)} - 10R_{BB}^2\rho_A^{(2)} - 6\rho_A^{(4)} + 6\rho_B^{(4)}]/10(4R_{AB}^2 - R_{BB}^2)$$

$$\sigma_B^{(2)} = \frac{(3R_{BB}^4 - 32R_{AB}^4)\sigma_B^{(0)} + 3R_{AB}^4\rho^{(0)} + 10R_{AB}^2\rho_A^{(2)} + 3\rho_A^{(4)} - 3\rho_B^{(4)}}{10(4R_{AB}^2 - R_{BB}^2)} \quad (\text{A.12})$$

AB₃ (point group = C_{3v})

$$\sigma_A^{(0)} = \frac{(3R_{AB}^2 - 2R_{BB}^2)\rho^{(0)} - 3\rho_A^{(2)} + 3\rho_B^{(2)}}{6R_{AB}^2 - 2R_{BB}^2}$$

$$\sigma_B^{(0)} = \frac{R_{AB}^2\rho^{(0)} + \rho_A^{(2)} - \rho_B^{(2)}}{6R_{AB}^2 - 2R_{BB}^2}$$

$$\sigma_A^{(2)} = [(6R_{BB}^4 - 48R_{AB}^4)\sigma_A^{(0)} + (9R_{AB}^4 - 6R_{BB}^4)\rho^{(0)} + 30R_{AB}^2\rho_B^{(2)} - 20R_{BB}^2\rho_A^{(2)} - 9\rho_A^{(4)} + 9\rho_B^{(4)}]/10(6R_{AB}^2 - 2R_{BB}^2)$$

$$\sigma_B^{(2)} = \frac{(6R_{BB}^4 - 48R_{AB}^4)\sigma_B^{(0)} + 3R_{AB}^4\rho^{(0)} + 10R_{AB}^2\rho_A^{(2)} + 3\rho_A^{(4)} - 3\rho_B^{(4)}}{10(6R_{AB}^2 - 2R_{BB}^2)} \quad (\text{A.13})$$

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