of Bader, Beddall, and Cade[1] (BBC) and Politzer.[3] The data show that the calculated charges are strongly dependent on the recipe used for apportioning electron density among atoms. The BBC charges are very different from those of the other three methods, which are in qualitative agreement.

To demonstrate the versatility of the charges from this electronegativity equalization procedure, we have plotted, in Figure 6, proton nmr chemical shifts[50] for CH_3X compounds against the hydrogen atom charges and, in Figure 7, ^{13}C nmr chemical shifts[51] for the hydrocarbons $(CH_3)_{4-n}CH_n$ against the carbon atom charges. The correlations are at least as good as those obtained with charges obtained by other techniques.

The term $\Sigma_{i \neq m} q_{ni}$ in eq 2 corresponds to the classical inductive effect. The fact that the coefficient for this term, unity, is small compared with the coefficients *b* and *c* indicates that the method predicts a rather small inductive effect. Chart I shows the calculated charges of the carbon atoms in *n*-octyl fluoride. The charge of a carbon atom in an infinitely long $-CH_2-$ chain is calculated to be −0.03346. By calculating the ratios of successive values of $Q_c + 0.03346$, we find that the inductive transmission coefficient for adjacent sp^3 carbon atoms is about 0.062. The discrepancy between this value and the commonly quoted[52] value of 0.33 is probably due to the fact that the latter value includes the "through space" field effect as well as the "through bond" inductive effect.

Chart I

Q_c		$Q_c + 0.03346$
	F	
0.08876	CH_2	0.12222
−0.02595	CH_2	0.00751
−0.03300	CH_2	0.00046
−0.03344	CH_2	0.00002
−0.03347	CH_2	−0.00001
−0.03351	CH_2	−0.00005
−0.03427	CH_2	−0.00081
−0.04655	CH_3	−0.01309

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Properties of Atoms in Molecules. V. An Easy Procedure for Estimating Atomic Charges from Calculated Core-Electron Energies[1]

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Abstract: Good linear relationships have been developed, for the atoms C, N, O, F, and Cl, between the charge on the atom when it forms part of a molecule and the calculated orbital energy of its 1s electrons. The charges used in obtaining these correlations were determined by a previously proposed integration procedure; with these relationships, however, it is now possible to estimate the atomic charges in many molecules simply by solving a set of simultaneous linear equations. Results are presented for a large number of molecules, and several cases are discussed in detail. The results for pyrazine and for lithium isocyanide are used to show how atomic charges computed by this method can help to understand and to predict chemical and physical properties of molecules.

Earlier papers in this series have presented and discussed a procedure for calculating the charge on an atom in a molecule directly from the molecular electronic density function.[3,4] This procedure has been applied to many diatomic and linear polyatomic molecules, and the results have been shown to be in good agreement with the properties of these molecules.[3–5]

Since these computations involve rather lengthy numerical integration, it would be desirable to have some alternate, simpler method for obtaining essentially the same results. It will now be shown that good estimates of these charges can be obtained for a large number of molecules by simply solving a set of linear simultaneous equations, provided that a good all-electron molecular orbital wave function is available for the molecule. The calculation of atomic charges then becomes a matter of a few minutes with a desk calculator.

Procedure

It has already been shown that the charges computed by numerical integration for fluorine in a series of diatomic fluorides and oxygen in a series of diatomic

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(1) A portion of this paper was presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 28, 1972.

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oxides correlate linearly with the energies of the molecular orbitals corresponding to the fluorine and oxygen 1s electrons in these molecules.[3b] The existence of such correlations suggested the possibility that similar ones could be developed for other atoms and then used to determine unknown atomic charges without the necessity of carrying out the numerical integration.

Since atomic charges have now been computed by the integration procedure for a large number of linear polyatomic molecules, sufficient data are available to investigate the charge *vs.* 1s orbital energy relationships for a total of five atoms: carbon, nitrogen, and chlorine, in addition to oxygen and fluorine. For each atom, a good linear relationship was obtained as long as only neutral molecules were considered. The points for molecular ions, however, such as OCN^- and SCN^-, fell far off the lines. It was apparent that a more refined treatment was needed if molecular ions were to be taken into account properly.

It has recently been shown that the orbital energy of the molecular orbital corresponding to the 1s electrons of an atom A (other than hydrogen or helium) can be written as the sum of an "internal" contribution, which should be insensitive to the environment, and an "external" contribution, which is, to a good approximation, equivalent to the electrostatic potential at nucleus A due to all of the other electrons and nuclei.[6] In principle, the latter potential should be evaluated using the wave functions of the other electrons. It can be well approximated, however, in terms of atomic charges.[10,11] The potential due to the electrons and nuclei of atoms other than A can be represented by the summation $\Sigma_{\mathrm{B}} Q_{\mathrm{B}}/R_{\mathrm{AB}}$, where Q_{B} is the net charge associated with atom B, and R_{AB} is the distance between nuclei A and B. The potential arising from the electrons on atom A (other than the 1s electrons) should be related to the electronic charge received by A from (or donated by A to) the other atoms in the molecule. Thus, this potential should be related to the net charge on A. According to this reasoning, therefore, the 1s orbital energy can be represented approximately by

$$\epsilon_{1s,\mathrm{A}} = k_{\mathrm{A}} Q_{\mathrm{A}} + \sum_{\mathrm{B}} Q_{\mathrm{B}}/R_{\mathrm{AB}} + C \qquad (1)$$

or equivalently

$$\epsilon_{1s,\mathrm{A}} - \sum_{\mathrm{B}} Q_{\mathrm{B}}/R_{\mathrm{AB}} = k_{\mathrm{A}} Q_{\mathrm{A}} + C \qquad (2)$$

It is relevant to note that relationships of the form of eq 2 have been widely and quite successfully used to correlate core-electron binding energies or binding energy shifts, determined by electron spectroscopy, with atomic charges computed by various methods.[12-17] In the present work, however, no attempt is made to equate experimental binding energies with calculated orbital energies;[18] the discussion deals exclusively with the latter.

The quantity k_{A} in eq 1 and 2 can be treated as a variable parameter. Alternatively, one may choose to identify it with either a nuclear-attraction integral, $\langle \phi_x(1)|1/r_{\mathrm{A}}|\phi_x(1)\rangle$, or an electron-repulsion integral, $\langle \phi_1(1)\phi_1(1)|1/r_{12}|\phi_x(2)\phi_x(2)\rangle$, where ϕ_x and ϕ_1 are, respectively, a valence shell atomic orbital on A and a 1s atomic orbital on A.[19,20]

If either of the latter two approaches is taken, but it is desired at the same time to preserve a relationship involving two variable parameters, then eq 1 may be modified to either

$$\langle \phi_x(1)|1/r_{\mathrm{A}}|\phi_x(1)\rangle Q_{\mathrm{A}} + \sum_{\mathrm{B}} Q_{\mathrm{B}}/R_{\mathrm{AB}} = \epsilon_{1s,\mathrm{A}} K_1 - C_1 \qquad (3)$$

or

$$\langle \phi_1(1)\phi_1(1)|1/r_{12}|\phi_x(2)\phi_x(2)\rangle Q_{\mathrm{A}} + \sum_{\mathrm{B}} Q_{\mathrm{B}}/R_{\mathrm{AB}} = \epsilon_{1s,\mathrm{A}} K_2 - C_2 \qquad (4)$$

All three of these approaches (*i.e.*, eq 2–4) were investigated. ϕ_x was taken to be the highest energy occupied orbital in the atom.[21] For each of the five atoms mentioned earlier, the atomic charges determined by the integration procedure and the 1s orbital energies for the same wave functions, which are of near-Hartree–Fock accuracy,[3,4] were used to test the linear relationships represented by eq 2–4. (In practice, these last two equations turn out to be nearly identical due to the very close similarity between the values of the nuclear-attraction integrals and the electron-repulsion integrals (Table I).[22]) Using the method of least squares, excellent linear correlations were obtained in all cases, as is shown by the correlation coefficients presented in Table II.[23]

These relationships were used to calculate the atomic charges for several test cases, using 1s orbital energies from extended-basis-set self-consistent-field molecular wave functions. These test cases were chosen to be molecules or molecular ions containing no atoms other than carbon, nitrogen, oxygen, fluorine, or chlorine; these are the atoms for which charge–energy equations were available. In each instance, the consistency of the calculated atomic charges could be assessed by noting

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(21) We are grateful to Dr. C. Froese-Fischer for providing the nuclear-attraction integrals and R. A. Donnelly for computing the electron-repulsion integrals (Table I).

(22) This indicates that, as far as electrostatic interaction is concerned, the valence electrons in these atoms see the 1s electrons as being very highly localized about the nuclei. The problem of core-electron–valence-electron interaction has been studied in detail by P. Politzer and K. C. Daiker, submitted for publication.

(23) A coefficient of 1.000 would correspond to an exactly linear correlation. See, for example, A. M. Neville and J. B. Kennedy, "Basic Statistical Methods for Engineers and Scientists," International Textbook Co., Scranton, Pa., 1964, Chapter 16.

Table I. Values (au) of Nuclear-Attraction and Electron-Repulsion Integrals[a]

Atom	$\langle\phi_x(1)\|1/r_A\|\phi_x(1)\rangle$	$\langle\phi_1(1)\phi_1(1)\|1/r_{12}\|\phi_x(2)\phi_x(2)\rangle$
C	0.77513	0.77594
N	0.94208	0.94743
O	1.1074	1.0984
F	1.2717	1.2563
Cl	0.73329	

[a] The nuclear-attraction integrals were obtained from the Hartree–Fock atomic wave functions of C. Froese, *J. Chem. Phys.*, **45**, 1417 (1966); the electron-repulsion integrals were evaluated using the Hartree–Fock–Roothaan atomic functions of E. Clementi, "Tables of Atomic Wave Functions," International Business Machines Corp., San Jose, Calif., 1965. The minor inconsistency involved in comparing quantities computed from these two different sets of atomic wave functions is completely unimportant in the present situation, since it introduces an average discrepancy of less than 1%. This does not in any way alter the statement, made in the text, that the values of the two types of integrals are very closely similar.

Table II. Correlation Coefficients for the Various Charge–Energy Relationships[a]

	Correlation coefficients		
Atom	Eq 2	Eq 3	Eq 4
C	0.9538	0.9679	0.9684
N	0.9695	0.9904	0.9904
O	0.9654	0.9770	0.9791
F	0.9954	0.9957	0.9966
Cl	0.9981	0.9967	

[a] The absolute values of the correlation coefficients are presented in this table, sinc ethese are what indicate the degrees of exactness of the correlations. The signs of the coefficients depend upon the slopes of the lines and would all be negative here.

Table III. Comparison of Atomic Charges Calculated with Various Relationships

Molecule or ion,	Calculated charges[a]								
	Equation 2			Equation 3			Equation 4		
AB	Q_A	Q_B	Sum	Q_A	Q_B	Sum	Q_A	Q_B	Sum
NF	+0.07	−0.08	−0.01	+0.08	−0.10	−0.02	+0.08	−0.09	−0.01
CN	+0.09	−0.18	−0.09	+0.12	−0.18	−0.06	+0.12	−0.18	−0.06
CN^+	+0.45	+0.31	+0.76	+0.67	+0.34	+1.01	+0.68	+0.34	+1.02
CN^-	−0.22	−0.54	−0.76	−0.38	−0.56	−0.94	−0.38	−0.56	−0.94
ClO	+0.09	−0.06	+0.03	+0.09	−0.09	0.00			
ClO^+	+0.48	+0.42	+0.90	+0.65	+0.47	+1.12			
ClO^-	−0.23	−0.53	−0.76	−0.38	−0.62	−1.00			

[a] The wave functions used in computing these charges are cited in Table VI.

how closely their sum approached the actual net charge (*e.g.*, zero for a neutral molecule). Some of these results are summarized in Table III. As could be anticipated (see Table I), eq 3 and 4 yield essentially identical charges. It is gratifying that the sum of these charges is usually very close to the desired net charge. The results obtained with eq 2, however, are often significantly different and are sometimes, considerably less consistent, particularly for molecular ions.

Accordingly, eq 3 was chosen as the most suitable for the extensive further applications which are intended. (It is preferred to eq 4 because of the easier evaluation of the one-electron integrals $\langle\phi_x(1)|1/r_A|\phi_x(1)\rangle$ compared with the two-electron integrals $\langle\phi_1(1)\phi_1(1)|1/r_{12}|\phi_x(2)\phi_x(2)\rangle$.)

In Table IV are listed the actual equations, of the type of eq 3, corresponding to each of the five atoms being considered. They are represented graphically in Figures 1 and 2. These expressions were used to determine the atomic charges in a large number of molecules, using the orbital energies of the molecular orbitals corresponding to the core (1s) electrons on the atoms; these energies were obtained from the best available extended-basis-set self-consistent-field molecular wave functions. For any molecule composed entirely of some combination of the atoms C, N, O, F, and Cl, or containing at most one differing atom, such as hydrogen, the charges can be computed simply by solving the appropriate set of simultaneous equations; in the latter case, the differing atom is handled by requiring the net charge on the molecule or molecular ion to have the correct value. For example, the equations to be solved for the molecule FOH are

$$1.2717Q_F + \frac{Q_O}{R_{FO}} + \frac{-(Q_F + Q_O)}{R_{FH}} = -1.6793\epsilon_{1s,F} - 44.3643$$

$$1.1074Q_O + \frac{Q_F}{R_{FO}} + \frac{-(Q_F + Q_O)}{R_{FH}} = -1.6504\epsilon_{1s,O} - 34.1931$$

If there are *two* differing atoms, or two nonequivalent forms of the same one (*e.g.*, the hydrogen in methylamine), then of course the present method is not strictly applicable. However, some approximation might be introduced to account for one of the extra charges. For instance, in the case of a hydrogen atom adjacent to a triple bond, one could make use of the fact that such hydrogens have generally been found, by the original integration procedure, to have charges in the range from +0.14 to +0.18; the only exception so far has been in the rather polar LiCCH molecule, in which the hydrogen charge is +0.10.[3a,4]

Table IV. Final Charge–Energy Relationships

Atom	Equation[a]
C	$0.77513Q_C + \Sigma_B Q_B/R_{CB} = -1.2784\epsilon_{1s,C} - 14.4729$
N	$0.94208Q_N + \Sigma_B Q_B/R_{NB} = -1.4536\epsilon_{1s,N} - 22.7995$
O	$1.1074Q_O + \Sigma_B Q_B/R_{OB} = -1.6504\epsilon_{1s,O} - 34.1931$
F	$1.2717Q_F + \Sigma_B Q_B/R_{FB} = -1.6793\epsilon_{1s,F} - 44.3643$
Cl	$0.73329Q_{Cl} + \Sigma_B Q_B/R_{ClB} = -1.5845\epsilon_{1s,Cl} - 166.194$

[a] Charges are in electron units, distances are in atomic units (1 au = 0.52917 Å), and energies are in atomic units (1 au = 27.2098 eV).

Results and Discussion

Before discussing the various atomic charges which have been calculated, an additional encouraging feature

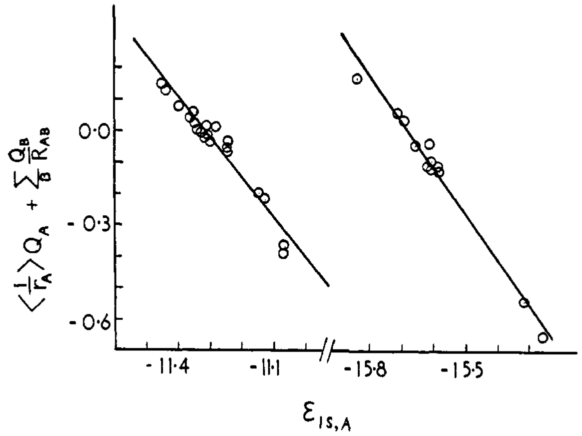

Figure 1. Atomic charges for carbon (left) and nitrogen (right), as obtained by integration procedure, plotted against 1s orbital energies in accordance with eq 3. Energies are in atomic units (1 au = 27.2098 eV).

of the equations in Table IV should be mentioned. If all of the charges, Q_A and Q_B, in any given one of these equations are set equal to zero, then the corresponding ϵ_{1s} should be the 1s orbital energy for atom A in the homonuclear diatomic molecule A_2. Table V compares the orbital energies predicted by the equations for zero charges with the self-consistent-field 1s orbital energies computed for the corresponding diatomic molecules. The agreement is excellent.

Table V. Orbital Energies (au) for Zero Charges

Atom, A	Orbital energy for zero charge[a]	SCF 1s orbital energy for molecule A_2[b]
C	−11.32	−11.36
N	−15.69	−15.68
O	−20.72	−20.73
F	−26.42	−26.42
Cl	−104.89	−104.90

[a] Calculated from equations in Table IV. [b] M. Krauss, "Compendium of *ab initio* Calculations of Molecular Energies and Properties," Technical Note 438, National Bureau of Standards, Washington, D. C., 1967.

In Table VI are summarized the charges which have been computed, using the method presented in the preceding section, for a large number of molecules, ranging in size from diatomic to the ten-atom pyrazine molecule. Some of the results are of particular interest and will be discussed in detail.

(a) CN, CN^+, and CN^-. As an additional test of the procedure being proposed, the charges in these three diatomic entities were determined by means of both the charge-energy correlations (Table IV) and also the original integration procedure. The agreement is very satisfactory (see Table VII).

(b) H_2O. In order to have some indication of how the charges calculated with the equations in Table IV depend upon the quality of the wave function, the results obtained for a series of H_2O wave functions built up from variously sized Gaussian orbital basis sets are given in Table VIII. The charge on the oxygen, as determined with the appropriate equation in Table IV, fluctuates over a range of about 0.3 eu, as does also the charge obtained by the well-known population analysis

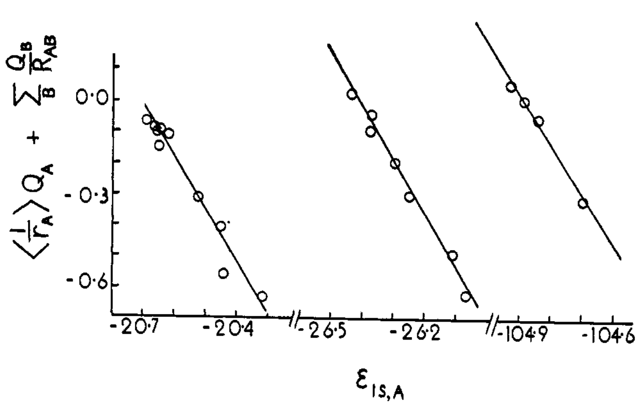

Figure 2. Atomic charges for oxygen (left), fluorine (middle), and chlorine (right), as obtained by integration procedure, plotted against 1s orbital energies in accordance with eq 3. Energies are in atomic units.

Table VI. Atomic Charges Calculated by New Procedure

Molecule or ion	Calculated charges			Ref for wave function
NF	N, +0.08	F, −0.10		*a*
NF^+	N, +0.84	F, +0.28		*a*
NF^-	N, −0.52	F, −0.39		*a*
OF	O, +0.05	F, −0.06		*b*
OF^+	O, +0.80	F, +0.32		*b*
OF^-	O, −0.61	F, −0.39		*b*
CN	C, +0.12	N, −0.18		*c*
CN^+	C, +0.67	N, +0.34		*c*
CN^-	C, −0.38	N, −0.56		*c*
PF	P, +0.19	F, −0.19		*a*
PF^+	P, +0.97	F, +0.03		*a*
PF^-	P, −0.66	F, −0.34		*a*
ClO	Cl, +0.09	O, −0.09		*d*
ClO^+	Cl, +0.65	O, +0.47		*d*
ClO^-	Cl, −0.38	O, −0.62		*d*
HF	H, +0.30	F, −0.30		*e*
HF_2^-	H, +0.21	F, −0.61		*e*
KrF	Kr, +0.10	F, −0.10		*f*
KrF^+	Kr, +0.81	F, +0.19		*f*
KrF_2	Kr, +0.52	F, −0.26		*g*
OF_2	O, +0.19	F, −0.08		*h*
HOF	H, +0.26	O, −0.13	F, −0.13	*h*
Li_2O	Li, +0.40	O, −0.79		*h*
H_2O	H, +0.25	O, −0.50		*i*
CH_4	C, −0.49	H, +0.12		*j*
NH_3	N, −0.69	H, +0.23		*k*
NH_4^+	N, −0.32	H, +0.33		*l*
BeF_2	Be, +1.10	F, −0.55		*m*
MgF_2	Mg, +1.55	F, −0.78		*m*
CaF_2	Ca, +1.84	F, −0.92		*m*
N_3^-	N_{end}, −0.72	N_{mid}, +0.36		*n*
SO_2	S, +0.59	O, −0.30		*o*
$C_4N_2H_4$	C, +0.27	N, −0.17	H, −0.18	*p*

[a] P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.*, **54**, 4563 (1971). [b] P. A. G. O'Hare and A. C. Wahl, *ibid.*, **53**, 2469 (1970). [c] P. E. Cade, private communication. [d] P. A. G. O'Hare and A. C. Wahl, *J. Chem Phys.*, **54**, 3770 (1971). [e] A. D. McLean and M. Yoshimine, "Tables of Linear Molecule Wave Functions," International Business Machines Corp., San Jose, Calif., 1967. [f] B. Liu and H. F. Schaefer III, *J. Chem. Phys.*, **55**, 2369 (1971). [g] P. S. Bagus, B. Liu, and H. F. Schaefer III, *J. Amer. Chem. Soc.*, **94**, 6635 (1972). [h] R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966). [i] J. W. Moskowitz and M. C. Harrison, *ibid.*, **43**, 3550 (1965). [j] E. Clementi and H. Popkie, *J. Amer. Chem. Soc.*, **94**, 4057 (1972). [k] P. Rajagopal, *Z. Naturforsch. A*, **20**, 1557 (1965). [l] M. Krauss, *J. Chem. Phys.*, **38**, 564 (1963). [m] E. F. Hayes, private communication. [n] S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **47**, 1953 (1967). [o] S. Rothenberg and H. F. Schaefer III, *ibid.*, **53**, 3014 (1970). [p] M. Hackmeyer and J. L. Whitten, *ibid.*, **54**, 3739 (1971).

Table VII. Comparison of Charges Calculated by Charge–Energy Correlations and by Integration Procedure[a]

Molecule or ion	Calculated charges Charge–energy correlations	 Integration procedure
CN	C, +0.12	C, +0.17
	N, −0.18	N, −0.17
CN^+	C, +0.67	C, +0.65
	N, +0.34	N, +0.35
CN^-	C, −0.38	C, −0.41
	N, −0.56	N, −0.59

[a] The wave functions were very kindly provided by Dr. P. E. Cade.

Table VIII. Calculated Charges for Various H_2O Wave Functions

Basis set[a]	Energy, au	Calculated charge on oxygen Present work	 Population analysis
(53/3)[b]	−75.5493	−0.78	−0.67
(53/31)[b]	−75.5919	−0.80	−0.40
(95/31)[b]	−76.0336	−0.50	−0.52
(952/32)[b]	−76.0421	−0.50	−0.63
(65/42)[c]	−76.0343	−0.47	

[a] All of the wave functions are in terms of Gaussian orbital basis sets. The notation (ABC/DE) indicates that the basis set consisted of A s-type, B p-type, and C d-type basis functions on the oxygen, and D s-type and E p-type basis functions on each hydrogen. [b] J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **43**, 3550 (1965). [c] C. D. Ritchie and H. F. King, *ibid.*, **47**, 564 (1967).

method.[24] It is encouraging, however, that the former reaches a steady value for the two best wave functions; the population analysis charge, on the other hand, still changes by 0.11 eu.[25] Furthermore, the charge calculated by the new procedure for another H_2O wave function, written in terms of a different Gaussian orbital basis set but giving nearly the same energy as the (95/31) function, is practically equal to the charge found for the latter (see Table VIII).

(c) Pyrazine, $C_4N_2H_4$. A particularly pleasing result was obtained for this 1,4-diazine. As indicated in Table VI, the carbons were found to be positive and the nitrogens and hydrogens negative. No population analysis is available for this wave function, but one has been carried out for another pyrazine function,[26] of slightly higher energy (−261.5543 *vs.* −262.2681 au). It yielded the opposite results; the computed charges were −0.12 for the carbons, −0.22 for the nitrogens, and +0.23 for the hydrogens. In order to ensure a valid comparison, the procedure being proposed in this paper was applied to this second wave function. Qualitatively the same results were obtained as with the better function: $Q_C = +0.40$, $Q_N = -0.21$, and $Q_H = -0.30$. Pyrazine is therefore a good test case, since the two methods of estimating atomic charges lead to opposite conclusions for the same wave function; the new procedure predicts positive carbons and negative hydrogens, while the population analysis indicates the reverse. It is accordingly very gratifying that the chemical behavior of pyrazine clearly supports the new charges. Pyrazine is quite susceptible to nucleophilic attack, but it is extremely *unreactive* toward electrophiles.[27] This is strongly indicative of positively charged carbons.

Table IX. Calculated Atomic Charges for Lithium Cyanide and Isocyanide

Molecule or ion	Calculated charges		
LiCN[a]	Li, +0.49	C, −0.28	N, −0.21
LiNC[a]	Li, +0.47	N, −0.41	C, −0.06
CN[b]		C, +0.17	N, −0.17
CN^-		C, −0.41	N, −0.59

[a] The wave functions used in calculating the atomic charges are from ref 28. [b] The atomic charges for CN and CN^- are taken from Table VII.

(d) LiCN *vs.* LiNC. The lithium cyanide (or isocyanide) molecule provides an interesting example of a rather unusual application of atomic charges. In an attempt to determine which of the two possible arrangements is the stable form of this molecule in the gaseous phase, Bak, *et al.*, computed near-Hartree–Fock wave functions for both possibilities and analyzed in detail the various contributions to their energies.[28] Since the calculated difference in energies was only 0.0141 au (8.8 kcal/mol, about 0.014% of the total energy), they could reach only a tentative conclusion, which was that LiNC is the more stable form. As a possible means of clarifying this situation, the atomic charges were computed for both forms, using the appropriate equations from Table IV. They are presented in Table IX, along with the integrated charges for CN and CN^-, taken from Table VII. These latter data indicate that in the process

$$\mathrm{CN} + e^- \rightleftharpoons \mathrm{CN}^-$$

58% of the charge transferred goes to (or comes from) the carbon.[29] This may be compared with what is calculated for, first, the processes

$$\mathrm{Li} + \mathrm{CN} \longrightarrow \mathrm{LiCN}$$

and

$$\mathrm{Li} + \mathrm{NC} \longrightarrow \mathrm{LiNC}$$

and second, the processes

$$\mathrm{Li}^+ + \mathrm{CN}^- \longrightarrow \mathrm{LiCN}$$

and

$$\mathrm{Li}^+ + \mathrm{NC}^- \longrightarrow \mathrm{LiNC}$$

In the first pair of reactions, 92% of the charge transferred from Li to CN is found to go to the carbon in forming LiCN and 49% in forming LiNC. The latter figure is clearly much closer to the 58% found for the simple electron attachment process

$$\mathrm{CN} + e^- \longrightarrow \mathrm{CN}^-$$

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(24) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(25) Atomic charges computed by the population analysis procedure are very sensitive to differences in basis sets, even for two wave functions with nearly the same energies and seemingly of the same quality (see ref 5).

(26) E. Clementi, *J. Chem. Phys.*, **46**, 4737 (1967).

(27) L. A. Paquette, "Principles of Modern Heterocyclic Chemistry," W. A. Benjamin, New York, N. Y., 1968, Chapter 9.

(28) B. Bak, E. Clementi, and R. N. Kortzeborn, *J. Chem. Phys.*, **52**, 764 (1970).

(29) Four of the five diatomic molecules for which data are available in Table VI have the property that when they gain an electron to form the negative molecular ion, the major portion of the additional unit of negative charge is acquired by the more positive (less electronegative) atom in the neutral molecule. The exception is ClO.

In the second pair of reactions, 25% of the charge transferred from CN^- to Li^+ comes from the carbon in producing LiCN and 66% in producing LiNC. Again, the latter is very considerably closer to the figure for

$$CN^- \longrightarrow CN + e^-$$

All of these numbers are only estimates, of course, and are computed from wave functions of differing degrees of accuracy. But the qualitative conclusion is clear; whether one views the formation of the molecule in terms of the interaction of Li with CN or Li^+ with CN^-, the nature of the charge transfer in forming LiNC is very much the more consistent with what has been found to be the charge-transfer behavior in the CN, CN^- pair. On this basis, therefore, one would predict, in agreement with Bak, *et al.*, that LiNC is the correct structure. Happily, a very recent study of isotopic infrared frequency shifts led to the same conclusion.[30,31]

(e) OF, OF_2, and HOF. The molecules OF and OF_2 are examples of the infrequently encountered situation in which an oxygen atom has a positive charge. This is consistent with the common assertion that oxygen is in a positive oxidation state in OF_2. The addition of a hydrogen to OF is sufficient to give the oxygen its usual negative charge.

Summary

The results and discussion presented in this paper indicate that the relationship which has been developed between atomic charges and 1s orbital energies can be used to obtain meaningful estimates of the charges on atoms in molecules. The requirements are an all-electron *ab initio* molecular orbital wave function for the molecule and the appropriate charge *vs.* energy equations for the individual atoms; the actual calculations are simply the solving of a set of simultaneous linear equations. As with other calculated properties, the results will be better and more consistent as the quality of the wave function improves.[32] Charge *vs.* energy equations have now been developed for five widely occurring atoms; additional atoms, such as phosphorus, sulfur, etc., will be included as more *ab initio* molecular orbital wave functions for molecules containing these atoms become available.[33]

Acknowledgment. We greatly appreciate the computational assistance of Dr. Bella Wang.

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[31] Clementi, *et al.*, have carried out another self-consistent-field calculation for this system, using a basis set even larger than that of ref 28. LiNC was again found to be the more stable form: E. Clementi, H. Kistenmacher, and H. Popkie, *J. Chem. Phys.*, **58**, 2460 (1973).

[32] The charge-energy relationships in Table IV were obtained using atomic charges computed with molecular wave functions of near-Hartree-Fock accuracy.[3,4]

[33] Two procedures for estimating atomic charges from experimentally determined, rather than calculated, inner shell energies have recently been proposed.[34,35] The charges obtained are based upon other definitions of atomic charge than that used in the present work, which has as its basis the molecular electronic density function.

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The Internal Chemical Shift. A Key to Bonding in Aromatic Molecules. I. Internal Shift Correlations

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Abstract: The study of proton shift behavior in nine families of disubstituted benzenes has provided quantitative correlations of internal and meta shifts among all families. The equations of correlation are useful in the prediction of shifts to an error of 0.015 ppm. The studies demonstrate shift additivity for the 4-substituted halobenzenes and suggest a chain rule relationship for substituent effects in those compounds. For that reason previous theories of substituent interactions involving inductive and resonance contributors appear incorrect when applied to proton shift data. In decreasing order of upfield shift at the ortho protons the substituents studied include $N(CH_3)_2$, NH_2, OCH_3, OH, F, CH_3, CH_2CH_3, H, Cl, $C(CH_3)_3$, Br, CN, $COOCH_3$, COOH, COCl, NO_2.

Initial high-resolution proton magnetic resonance studies of substituted benzenes by Dailey[2] gave evidence that substituent effects on the chemical shifts of ring protons were predictable although not well behaved. Subsequent reports by Diehl,[3] Dailey,[4] Smith,[5] Beachell and Beistel,[6] Reed,[7] and others suggested that trends in the shifts of aromatic protons (relative to benzene) paralleled trends in Hammett σ constants[8] and electronegativities.[9] But in no case were the confidence limits high for correlations with those parameters. Because no apparent relationships existed

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