Properties of atoms in molecules: Atomic polarizabilities

Keith E. Laidig and Richard F. W. Bader

ARTICLES YOU MAY BE INTERESTED IN

Properties of atoms in molecules: Atomic polarizabilities

Keith E. Laidig and Richard F. W. Bader

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

The theory of atoms in molecules is applied to the determination of the atomic and group contributions to the molecular polarizability in diatomic and polyatomic systems, covering a wide range of atomic interactions. The calculations are performed through the use of coupled-perturbed Hartree–Fock theory. An applied field polarizes the atomic charge distributions and induces a transfer of charge between them. The resulting changes in the dipole moment per unit applied field determine the corresponding contributions to the polarizability. In general, the component of the polarizability along the internuclear axis in a linear molecule or in the direction of a chain of bonds in a nonlinear polyatomic molecule, exceeds the perpendicular component because of the transfer of electronic charge between the two ends of the molecule, between the methyl groups in ethane, and between the methylene groups in ethene, for example. Atoms shielded from an applied field, carbon in methane for example, polarize in a direction counter to that of the applied field, responding instead to the opposing field created by the transfer of charge between the exterior atoms. The same behavior is found in vibrationally induced polarizations of a molecular charge distribution. The extent of atomic polarization and of interatomic charge transfer caused by an external field are readily related to known properties of the atomic charge distributions and the corresponding contributions to the polarizability may be understood and predicted. The mean molecular polarizability and its group contributions are found to be linearly proportional to the corresponding sum of atomic volumes, making possible the prediction of molecular polarizabilities from tabulated atomic volumes as determined by the theory of atoms in molecules.

I. INTRODUCTION

The polarizability of an atom in a molecule is a concept which has long been used in the prediction and understanding of chemical reactivity and intermolecular interactions. The essential idea is the equating of α, the polarizability of a molecule, to a sum of atomic or bond contributions.[1] There is a history of attempts to assign atomic and group contributions to the measured refractive index, and on the basis of these results, to assign corresponding contributions to the molecular polarizability (see Ref. 1 for a review). Particular impetus for the partitioning of α comes from the study of the intensities of Raman spectra. Wolkenstein[2] formulated a theory for the calculation of polarizability derivatives based on the assumption that α can be expressed as a sum of bond contributions which are diagonal in their respective bond coordinate systems. This and other models relating α and its derivatives to atomic and bond contributions have been the subject of a number of reviews.[3,4] Applequist[5] has proposed an empirical partitioning of α into atomic contributions wherein an attempt is made to take into account the manner in which the field arising from the polarization of one atom contributes to the polarizability of the others in terms of a dipole–induced dipole model. It is the inadequate handling of these internally induced contributions to the polarizability or their complete omission, that constitutes the weakness of the empirical approaches. Stone[6] has defined a charge susceptibility, which contains the information needed to determine any of the molecular polarizabilities. This quantity is stated in terms of the first-order correction to the charge density which results from a δ-function change in the elec-trostatic potential at a point in space. Such an approach takes into account the effect which the field throughout the molecule has on an associated property at any one point. This approach has been applied to the determination of what Stone calls distributed polarizabilities,[6] wherein the total polarizability is equated to the sum of contributions from disjoint spatial regions, the boundaries of the regions being determined arbitrarily.

The molar polarization, as determined by the dielectric constant in the Clausius–Mosotti equation or by the molar refraction, has the dimensions of volume and modeling an atom by a sphere of constant electronic charge density yields an expression for its polarizability proportional to its volume. Thus one associates large polarizabilities with molecules that have loosely bound charge density and relatively large volumes. Attempts to correlate the polarizabilities of atoms and ions with their volumes using Paulings "univalent" radii are not that satisfactory.[7] Using such radii, both the refractivities and polarizabilities of atoms and ions are better related to the radius raised to the power 4.5.[1] Gough,[8] however, has demonstrated a good correlation of the mean molecular polarizability for a number of hydrocarbon molecules together with H_2 and CO, with the molecular volumes assigned using the theory of atoms in molecules. This correspondence is further illustrated in this paper.

The theory of atoms in molecules[9,10] demonstrates that the total polarizability of a molecule is, as are all molecular properties, expressible as a sum of atomic contributions and in this paper the atomic and group contributions to the polarizability are determined and discussed for a variety of molecules. Since all atomic properties are determined by the-

ory, including atomic volumes,[11] it is possible to investigate the basis of the various models that have been proposed in the past and, with the increased understanding afforded by the quantum description of an atom in a molecule, to establish new and more realistic models of molecular polarizability. It is found that atoms internal to a system, such as carbon in methane, polarize in a direction opposite to that of the applied field and their contribution detracts from the overall polarizability of the molecule. This same behavior is found for the same atoms in vibrationally induced polarizations of a molecular charge distribution[12] and thus one finds that an atom in a given bonding situation exhibits a characteristic response to a field whether it be internally generated or externally applied.

An atom in a molecule is an open quantum system[9,10] which satisfies the boundary condition of exhibiting a zero flux in the gradient vector field of the charge density at every point of its surface $S(\mathbf{r})$,

$$\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) = 0, \quad \forall\mathbf{r}\in S(\mathbf{r}). \tag{1}$$

This boundary condition appears as a constraint in the generalized variation of the quantum action integral or of Schrödinger's energy functional in the case of a stationary state,[13] to obtain corresponding atomic statements of the principle of stationary action, a principle which has also been shown to apply when the system is in the presence of an electromagnetic field.[14] For a system in a stationary state, this variation principle yields Schrödinger stationary state equation, for which the natural boundary condition is

$$\nabla_i\Psi\cdot\mathbf{n}(\mathbf{r}_i) = 0 \tag{2}$$

and the principle of stationary action for the open system, i.e., atom Ω,

$$\delta G[\Psi,\Omega] = 1/2\{(i/\hbar)\langle[\hat{H},\hat{F}]\rangle_\Omega + \text{c.c.}\}, \tag{3}$$

In Eq. (3), $G[\Psi,\Omega]$ is Schrödinger's energy functional and $\hat{F}$ denotes an operator which induces the infinitesimal change in the state function and hence in G. This equation is a variational statement of the hypervirial theorem and it applies to any region of space of Ω bounded by a surface which satisfies Eq. (1). Equation (3) serves to define the observables, their average values and the theorems such as the virial and Ehrenfest theorems, which determine the mechanics of a system in a stationary state. For a bound system, Eq. (2) is satisfied for any $r_i = \infty$ and thus Schrödinger's equation is obtained for the total system. Equation (1) however, is satisfied by the total system and by every atom within the system. Thus the average properties and mechanics of the atoms, as well as those of the total system, are predicted by quantum mechanics through Eq. (3).

The manner of averaging an observable over an open system, as denoted by the symbol $\langle\ \rangle_\Omega$ is determined by the principle of stationary action, Eq. (3). It requires a summation over all spin coordinates and an integration over the spatial coordinates of all electrons but one, a process denoted by $\int d\tau'$ and one which yields a corresponding property density. Thus the property density at a point in space is determined by the appropriate average over the motions of all the particles in the system and integration of the property density over the basin of the atom yields its atomic value. Atten-

tion has been drawn to the fact that a property density resulting from a molecule being placed in an external field must describe how the perturbed motion of the electron at $\mathbf{r}$ depends upon the field strength everywhere inside the molecule,[6] a requirement that is met by the open system averaging of an observable. The averaging also meets the second necessary requirement of an atomic property, that the sum of the atomic contribution equals the average value of the property for the molecule. The property density of present interest, the polarizability density, is defined as[15]

$$\begin{aligned}\alpha(\mathbf{r}) &= -e\mathbf{r}\rho^{(1)}(\mathbf{r}) \\ &= -eN\int d\tau'(\Psi^{(0)*}\mathbf{r}\Psi^{(1)} + \Psi^{(1)*}\mathbf{r}\Psi^{(0)}),\end{aligned} \tag{4}$$

where $\rho^{(1)}(\mathbf{r})$ is the first-order correction to the electron density distribution. The basin contribution to the atomic polarizability tensor is

$$\alpha_b(\Omega) = \int_\Omega \alpha(\mathbf{r})d\mathbf{r}, \tag{5}$$

which yields the molecular polarizability when summed over the atoms in a molecule

$$\alpha = \sum_\Omega \alpha_b(\Omega). \tag{6}$$

The explicit dependence of the polarizability density $\alpha(\mathbf{r})$ on the effect which the field has over the entire molecule is further discussed and illustrated in Ref. 14.

The calculations were performed using coupled perturbed Hartree–Fock theory as contained in the program GAUSSIAN 88[16] using the $[5s4p/3s]$ Dunning contractions[17(a)] of the $(11s6p/5s)$ Huzinaga basis[17(b)] complemented with two d functions for the heavy atoms and two p functions for the hydrogens whose exponents were adjusted slightly in accordance with the suggestion of Duijveldt.[17(d)] This is the basis Gough[8] found to be satisfactory for the determination of the polarizability and its derivatives in a series of hydrocarbon molecules. The molecules under study here are H_2, N_2, F_2, CH_4, NH_3, H_2O, HF, HCl, CO, CO_2, LiH, LiF, C_2H_6, and C_2H_4. These same molecules have been studied by others[18–23] using a range of basis sets and studying separately the effects of electron correlation on the polarizability. The Dunning set used here is slightly superior in its estimates of α to the largest set studied by Spackman,[23] the 6-31G** set[24] with values for the polarizing functions determined by optimizing the calculated value for α and augmented with diffuse s functions on all centers. The results obtained here are in good agreement with those obtained by others at the perturbed SCF level of calculation, calculations which are more than adequate to describe the observed trends and values in the polarizability, as is the purpose of this investigation. Correlation is necessary to obtain full quantitative agreement with experiment and to recover accurately the anisotropy in α, although the results reported here always give the correct ordering of the magnitudes of the principal components.

II. EFFECT OF AN ELECTRIC FIELD ON AN ATOMIC BASIN AND ITS SURFACE

The application of an electric field perturbs the distribution of charge over the basin of the atom and, because of the associated changes in the gradient vector field, the surface of the atom is also perturbed. This is illustrated in Fig. 1 for H_2 and for a number of other molecules in Fig. 2, for a field applied parallel to the internuclear axis. There is a transfer of

electronic charge from one atom or grouping of atoms to the other in the direction of the field as indicated by the positive values for the changes in the atomic or group population denoted by $\Delta N(A)$, Table I. The changes in molecular properties listed in Table 1 are for a field directed from B to A and all quantities are divided by the field strength to give the change per unit field. The transfer of charge induced by the applied field causes a shift in the $(3, -1)$ or bond critical point as indicated by the values of $\Delta r_b(A)$, where $r_b(A)$ is the distance of the bond critical point from the A nucleus. The charge density attains its minimum value along the
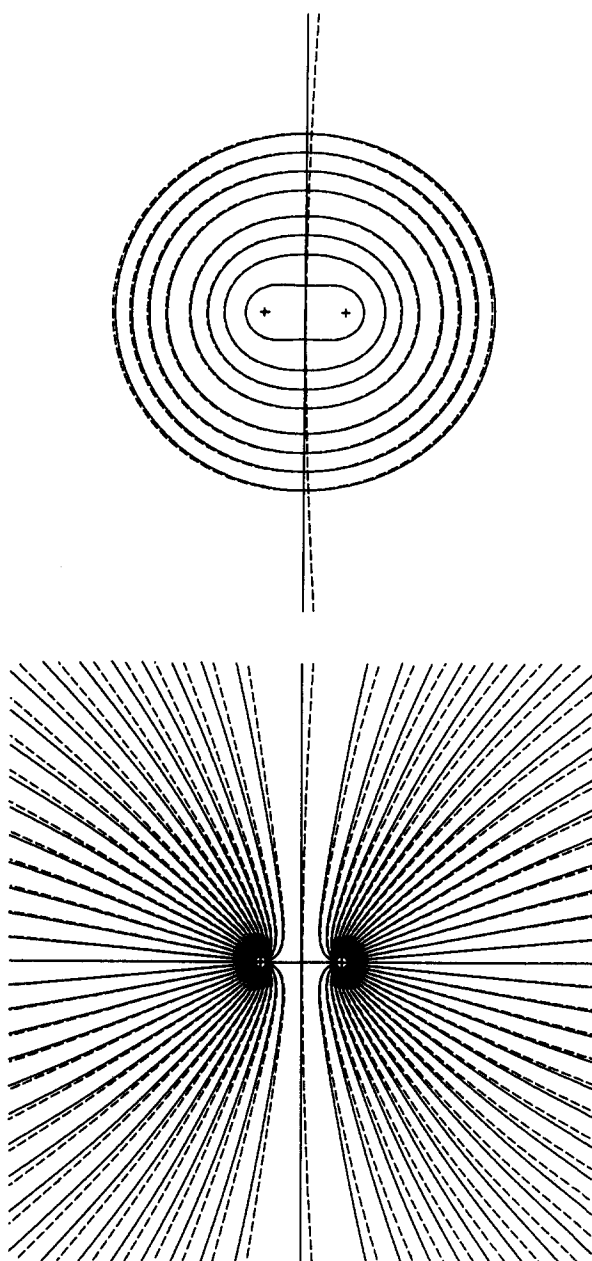

FIG. 1. Contour map of the charge distribution of ground state H_2 for field free case (solid contours) and for a positive field applied along the internuclear axis in the direction right to left (dashed contours). The lower diagram illustrates the corresponding perturbation of the gradient vector field of the charge density. Note that the contours are displaced in the direction of the field while all gradient paths of the charge density, including those defining the interatomic surface, are displaced in a direction counter to the direction of the field. Outer contour value is 0.001 a.u. and remaining contours increase in value 2×10^n, 4×10^n, 8×10^n a.u. beginning with $n = -3$.
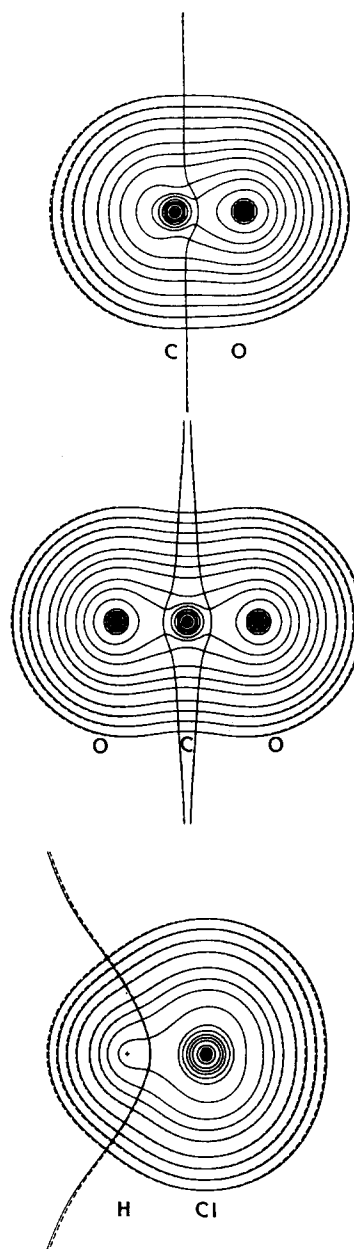
FIG. 2. Contour maps of the charge distributions of ground state carbon monoxide, carbon dioxide, and hydrogen chloride for the field free case (solid contours) and for a field applied along the internuclear axis. The contours (same values as in Fig. 1) are displaced in the direction of the field. The bond critical point and interatomic surface are displaced in a direction counter to the field direction in HCl. The corresponding displacements in CO and CO_2 are many times smaller (Table I).

TABLE I. Effect of external field on bond critical point and atomic surface: all changes are per unit applied field.[a]

AB	ρ_b	$\nabla^2\rho_b$	Δr_b(A)	$\Delta\rho_b^e$	ΔN(A)	$\Delta\upsilon$(A)	$\Delta\upsilon$(B)	υ(AB)[b]	α Calc.	α Exp.[d]
H–H	0.2755	− 1.2898	+ 1.017	− 3.3(− 3)	4.161	285	− 275	119.2	4.95	5.44
N–N	0.7237	− 3.0361	+ 0.058	− 1.2(− 5)	5.413	455	− 406	233.0	11.01	11.78
F–F	0.3510	+ 0.1771	+ 0.965	− 8.5(− 3)	3.750	128	− 92	185.7	7.69	
H₃C–CH₃	0.2531	− 0.6750	+ 3.641	− 1.9(− 2)	6.826	320	− 403	434.9	26.92	30.4
H₂C–CH₂	0.3688	− 1.2886	+ 0.858	− 6.0(− 4)	9.736	672	− 694	389.0	26.34	28.4
H–C(CH₄)	0.2885	− 1.0998	+ 2.095	− 2.6(− 1)	5.059	250	− 18	280.1	15.73	17.5
H–N(NH₃)	0.3590	− 1.8971	+ 1.297	− 1.6(− 2)	3.615	189	− 141	233.5	12.33	15.0
H–O(H₂O)	0.3906	− 3.0057	+ 0.830	+ 2.1(− 1)	1.541	133	− 180	186.3	8.14	9.922
H–F	0.3920	− 3.6382	+ 0.459	+ 3.2(− 1)	1.387	98	− 53	141.6	4.70	5.60
H–Cl	0.2632	− 0.9451	+ 1.881	− 1.7(− 2)	4.441	209	− 345	274.3	15.92	17.6
Li–H	0.0316	+ 0.1578	− 0.403	+ 5.1(− 2)	1.562	255	449	231.7	21.86	
Li–F	0.0778	+ 0.7063	− 0.187	+ 5.6(− 2)	0.372	33	329	178.8	6.98	
C–O	0.5111	+ 1.1766	− 0.003	+ 6.1(− 2)	3.009	212	28	244.0	11.96	13.4
C–O(CO₂)	0.4864	+ 3.7220	+ 0.053	+ 9.1(− 2)	3.045[c]	28	234 − 144[b]	293.4	15.30	17.6

[a] Field direction is A⁺ B⁻, i.e., B to A along the indicated internuclear axis; all quantities in atomic units.
[b] Volumes are for 0.001a.u. envelope of density.
[c] Value given is for oxygen atoms as $\Delta N(C) = 0$.
[d] From Ref. 31.
[e] Bracketed number is exponent in 10^{-n}.
[f] For oxygen at negative end of field.

bond path at the (3, − 1) critical point and this point serves as the terminus of the trajectories of $\nabla\rho$ which define the interatomic surface. Thus the transfer of charge also results in a shift in the interatomic surface. A shared interaction (H₂ to HCl in Table I) is one in which the value of ρ at the bond critical point, ρ_b, is relatively large and $\nabla^2\rho_b < 0$, the latter indicating that the interaction is dominated by the contraction of ρ towards the bond path leading to a concentration of electronic charge in the interatomic surface and to a shared accumulation of charge in the internuclear region.[25] For the shared interactions the interatomic surface does not shift in the direction of the field. Instead, the transfer of charge to atom A causes the bond critical point and the interatomic surface to shift towards B, that is in a direction counter to the direction of the applied field, the accompanying transfer of electronic charge serving to enlarge the basin of the downfield atom. The shift in the bond critical point together with the extent of charge transfer to the hydrogens in the hydrides H_nX (Table I) caused by the application of the field decreases as the electronegativity of X increases. The decrease in the shift of the bond critical point parallels the increase in the tightness of the binding of the electronic charge in the internuclear region as determined by an increase in the value of ρ_b and the decrease in $\nabla^2\rho_b$. The contraction and concentration of the electronic charge towards and along the bond path increases as $\nabla^2\rho_b$ decreases in value because of the increase in the magnitude of the perpendicular curvatures of ρ.

The volume of an atom is determined by the intersection of the atomic surface with an envelope of the charge density of some chosen value.[11,26] The 0.001 a.u. envelope for an entire molecule has been found to give good agreement with the van der Waals shapes and sizes of molecules in the gas phase. The volume of A increases with the applied field for all of the shared interactions because of the shift in the sur-

face and because of the displacement of the outer density contours in the direction of the field (Figs. 1 and 2). The volume of B undergoes a corresponding decrease. In general, the outer contours on A are extended away from the interatomic surface by the applied field to a greater extent than the corresponding contours on B are contracted towards it.

For ionic and intermediate atomic interactions (LiH, LiF and CO, CO₂ in Table I), the bond critical point shifts in the direction of the applied field. In an ionic interaction, ρ_b is relatively small in the value and $\nabla^2\rho_b > 0$, indicating that electronic charge is removed from the region of the interatomic surface and concentrated separately in each atomic basin. In the very polar intermediate atomic interactions present in CO and CO₂, ρ_b is large and charge is accumulated in the interatomic surface, but the interaction is dominated by the contractions of the density towards each nucleus as measured by the dominant positive curvature of ρ along the bond axis. This curvature attains its largest value for CO and correspondingly, this molecule exhibits the smallest shift in its interatomic surface. The volume changes for A are dominated by the displacements of the outer density contours and $\Delta\upsilon(A) > 0$ in spite of the adverse shift in the interatomic surface, a shift which also makes $\Delta\upsilon(B) > 0$.

Carbon of CO exhibits a relatively large change in atomic volume in an applied field, one which increases to 306 a.u. when the field is reversed. The reason for this is made evident by the contour display for CO in Fig. 2. There is a large diffuse distribution of nonbonded charge on the carbon atom whose radius is considerably greater than that for an isolated carbon atom. This behavior is typical of an interaction in which the number of valence electrons on the donor atom A exceeds the number of vacancies on the acceptor B. The remaining relatively loose bound valence density on A is strongly polarized into its nonbonded region as a consequence of the net negative field exerted by B. This charge

concentration dominates the properties of CO, being the cause of its relatively large polarizability, its reactivity as a Lewis base and, as discussed below, the reason for the near vanishing of its dipole moment.

A large change in atomic volume in response to an applied field should be indicative of a large atomic contribution to the molecular polarizability and this is indeed the case, as is demonstrated below. One anticipates from the value for $\Delta v(H)$ for LiH that the hydride ion makes a substantial contribution to a molecular polarizability. Table I also lists the total molecular volumes as determined by the 0.001 a.u. charge density envelope[11,26] and the mean polarizability $\bar{a}$, equal to the average of the trace of α. Plots of the experimental and calculated values of $\bar{a}$ versus the molecular volume yield good linear relationships, Fig. 3. The observed linear relationship is quite exceptional when one takes into account the great diversity in the atomic interactions represented by this series of molecules, covering as they do the complete spectrum of bonding. The only serious exception is LiH for which no experimental value is known, but a high level calculation[21] predicts the value of $\bar{a}$ to be 29.3 a.u.
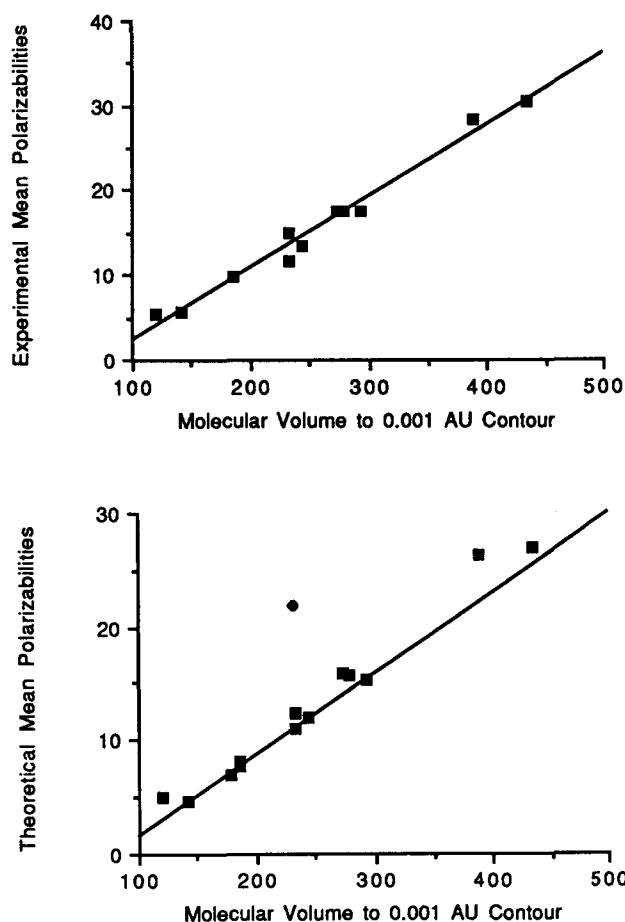

FIG. 3. Mean molecular polarizabilities, experimental and theoretical, plotted versus the molecular volumes determined by the 0.001 a.u. envelope of the electronic charge density which yield correlation coefficients of 0.980 and 0.977, respectively. The point lying well off the line in the theoretical case is for LiH and this value is excluded in the determination of the correlation coefficient. The use of the 0.002 a.u. density envelope for the determination of the molecular volumes yields slightly poorer linear relationships.

It is possible to separate the change in an atomic population $\Delta N(\Omega)$ caused by an applied field into two contributions; one arising from the transfer of charge from one atomic basin to another $\Delta N_b(\Omega)$, and the other from the shift in the interatomic surface $\Delta N_s(\Omega)$. The average atomic population in the presence of the field $N_f(\Omega)$, is given by

$$N_f(\Omega) = \int_{\Omega_0 + \delta\Omega} (\rho_0 + \rho^{(1)})d\tau, \tag{7}$$

where ρ_0 is the unperturbed density, $\rho^{(1)}$ is the first-order correction to the density, Ω_0 is the basin as determined by ρ_0, and $\delta\Omega$ is the change in the atomic basin caused by the shift in interatomic surface. Retaining terms to first order, the atomic population in the presence of the field is

$$N_f(\Omega) = \int_{\Omega_0} \rho_0 \, d\tau + \int_{\Omega_0'} \rho^{(1)} \, d\tau + \int_{\delta\Omega} \rho_0 \, d\tau$$

$$= N_0(\Omega) + \Delta N_b(\Omega) + \Delta N_s(\Omega) \tag{8}$$

and the change in the atomic population caused by the application of a field, $\Delta N(\Omega) = N_f(\Omega) - N_0(\Omega)$, is equal to the contribution of the perturbed density to the basin of the atom $\Delta N_b(\Omega)$, and to the contribution of the unperturbed density to the change in volume resulting from the shift in atomic surface, $\Delta N_s(\Omega)$. These contributions to the change in the total atomic population per unit field strength for a number of molecules are given in Table II together with their associated contributions to the basin and surface polarizabilities of the atoms, results which are discussed below.

III. ATOMIC CONTRIBUTIONS TO THE DIPOLE MOMENT AND ITS CHANGE

The polarizability of a molecule is the proportionality constant α which relates the first-order change in the dipole moment to an applied electric field,

$$\Delta\mu = \mu^{(1)} = \alpha\mathscr{E}. \tag{9}$$

The dipole moment for a system with nuclear charges Z_α with position vectors X_α and a charge density $\rho(r)$ is

$$\mu = \sum_\alpha Z_\alpha X_\alpha - \int r\rho(r)d\tau. \tag{10}$$

The change in dipole moment generalized to include changes in the nuclear position coordinates as well as in the charge density, is

TABLE II. Basin and surface contributions to polarizability: all changes per unit field.[a]

AB	$\Delta N_s(A)$	$\Delta N_b(A)$	$\alpha_s(A) = \alpha_s(B)$	$\alpha_b(A)$	$\alpha_b(B)$
H–H	+ 1.88	2.28	− 0.032	3.166	3.166
N–N	+ 1.31	4.10	− 0.006	7.113	7.113
$H_3C–CH_3$	+ 3.03	3.80	− 0.177	14.492	14.492
$H_2C–CH_2$	+ 2.61	7.13	− 0.058	17.689	17.689
H–F	+ 0.67	0.72	+ 1.209	1.699	3.797
H–Cl	+ 1.89	2.55	+ 3.728	7.246	10.329
Li–F	− 0.12	0.49	− 0.162	1.317	6.108

[a] Field direction is B to A; all quantities in atomic units.

$$\Delta\mu = \sum_\alpha Z_\alpha \Delta X_\alpha - \int r\rho^{(1)}(r)d\tau \cdot \mathscr{E}. \tag{11}$$

Both expressions are independent of the choice of origin for a neutral molecule. Equations (10) and (11) can be expressed in terms of a sum of atomic contributions using the atomic charges $q(\Omega)$,

$$q(\Omega) = Z_\Omega - \int_\Omega \rho_0(r)d\tau = Z_\Omega - N(\Omega) \tag{12}$$

and first moments $M(\Omega)$,

$$M(\Omega) = - \int_\Omega r_\Omega \rho_0(r)d\tau, \tag{13}$$

where $r_\Omega = r - X_\Omega$. Using these definitions, the dipole moment can be expressed as a sum of a charge transfer and an atomic polarization contribution for each atom

$$\mu = \sum_\Omega [q(\Omega)X_\Omega + M(\Omega)] = \mu_c + \mu_p \tag{14}$$

and both contributions can be separately summed to yield a charge transfer term μ_c and a polarization term μ_p which are generally of opposite sign.[12,27] Similarly, a change in a dipole moment expressed as a sum of atomic contributions is

$$\Delta\mu = \sum_\Omega \{[\Delta q(\Omega)X_\Omega + Z_\Omega \Delta X_\Omega] + \Delta M(\Omega)\}$$

$$= \Delta\mu_c + \Delta\mu_p \tag{15}$$

showing that to first order, the charge transfer term can be changed by a change in $q(\Omega)$ or in X_Ω.

The polarizability is determined analytically by GAUS-SIAN 88[16] using the procedure for obtaining the derivatives of a Hartree–Fock result developed by Pople et al.[28] This series of programs also calculates the polarizability numerically by determining the change in dipole moment caused by the application of a finite field. In the analytical method the derivatives of the density matrix are evaluated for the limiting case of zero field. To obtain perturbed charge densities which can be used to determine the changes in the atomic moments, the derivative terms were multiplied by a field of strength 0.009 449 a.u. the value used in the accompanying numerically based programs. Division of the change in population and first moment by the field then yields the desired contributions to the atomic polarizability. When the molecule does not possess a plane of symmetry perpendicular to the applied field, as for example is the case for a field applied along the symmetry axis in ammonia or water, the magnitude of the induced dipole moment depends upon the field direction. In such cases an average value over both field directions is taken to obtain the polarizability, the procedure followed in the numerical program. The deviation from linear behavior for the field strength used here is large only for H in LiH and Cl in HCl. These atoms undergo very different volume changes per unit field, 125 and 57 a.u., respectively, and consequently, very different atomic polarizations, upon reversal of the direction of the field. They will also exhibit significant hyperpolarizabilities. The polarizabilities obtained numerically generally agree with those obtained analytically to within

0.02 a.u. or less. Summing the atomic contributions, which are determined by numerical integrations, to obtain the total polarizability yields values which in general differ by 0.02 a.u. or less from the analytically determined values with the exceptions of the ionic systems LiH and LiF. These molecules present difficulties in the numerical integrations because of their small charge transfer. The results reported for these two molecules are for a single direction of the axial field. There is a residual error of 0.15 a.u. in $\alpha_\perp$ for LiH.

One can determine the separate basin and surface contributions to an atomic polarizability. Integration of the unperturbed density and of this density weighted by the position vector r_Ω over the perturbed basin of the atom enables one to calculate the charge transfer and change in polarization resulting from the shift in the interatomic surface and their associated contributions to the polarizability, $\alpha_s(\Omega)$. Results of such calculations are given in Table II. Since $\alpha_s(A) = -\alpha_s(B)$ for a given principal axis, one can also obtain the basin and surface contributions to an atomic or group polarizability for a field direction perpendicular to a symmetry plane coincident with an interatomic surface by the respective averaging of the sum and difference of the two polarizabilities. The surface contributions to the atomic or group polarizabilities in the homonuclear diatomics and ethylene are relatively small in magnitude as a result of the near cancellation of the charge transfer and polarization contributions resulting from the shift in the surface. The surface contributions cancel when the results are averaged over both directions of the applied field.

While the total charge transfer contribution μ_c or its change $\Delta\mu_c$, are origin independent, each atomic contribution to these terms depends upon the choice of origin. Thus the atomic polarizabilities reported in Table II depend upon the choice of origin which was taken as the center of mass. One knows from experiment however, that it is possible to assign moments and polarizabilities to groupings of atoms and for this to be possible the group contribution to μ or α must be origin independent. The atomic contributions to the dipole or the polarizability recover this property when they are combined to yield corresponding group contributions. Let q_i denote the net charge or the change in the net charge of atom Ω_i. Because of the constraint that the sum of the atomic charges or of the changes in these charges must vanish, one can express the sum over the $q_i(\Omega)$ or $\Delta q_i(\Omega)$ in the charge transfer term, for a linked sequence of atoms or grouping of atoms, as a sum of origin independent terms

$$\sum_i^n q_i X_i = \sum_i^{n-1} q_i'(X_i - X_{i+1}), \tag{16}$$

where

$$q_i' = \sum_j^i q_j \tag{17}$$

is the net charge or the change in the net charge for a group containing the atoms $j = 1$ to i. Any of the q_i' can itself be a sum of net charges over other groups linked to atom i. In this way the result can be applied to any structure. As an example, the charge transfer contributions from a methyl group can be expressed as

$$\sum_{\Omega} q(\Omega)X_{\Omega} = \sum_{k} q(H_{k})(X_{k} - X_{c}) + q'_{c}X_{c}, \qquad (18)$$

where q'_c is the net charge on the methyl group. If there is no transfer of charge between the methyl group and the remainder of the system, then this group is decoupled from the remainder of the system. If q'_c or $\Delta q'_c$ is different from zero, then the term $q'_c(X_c - X_R)$ or $\Delta q'_c(X_c - X_R)$, which represents the contribution from the transfer of charge between methyl and the remainder of the system or the change in this quantity, is included in the group contribution. Any or all of the charges $q(H)$ could themselves denote the net charge for a group attached to the carbon atom.

The atomic terms can be combined to yield contributions for any group of interest and in this manner one can obtain a prediction and understanding of the nature of the contribution of a given group to the dipole moment or polarizability of a molecule. Whether or not the contribution of a given group to μ or α is transferable between systems can be predicted and understood.

Table III lists the atomic polarization and charge transfer contributions to the molecular dipole moments. A knowledge of the atomic contributions to the dipole moment of the unperturbed molecule enables one to better understand the changes induced by an applied field. The origin independent charge transfer contribution for a group A–B is given by $q_A(X_A - X_B)$, which is the total such contribution for a diatomic molecule. There is a transfer of close to one electron in the ionic systems LiH and LiF and their dipole moments are dominated by the charge transfer term μ_c which is close to the limiting value of $- eR$. The atoms are both polarized in a direction counter to the direction of

charge transfer and the atomic polarizations reduce the magnitudes of the final moments. As anticipated, the atomic polarization contributions are smallest for the tightly bound cations while that for hydrogen in LiH is over twice that for fluorine in LiF.

There is a substantial transfer of charge from carbon to oxygen in CO and an almost equal amount is transferred to each of the oxygen atoms in CO_2.[29] Thus the contribution to $\mu(CO)$ resulting from the transfer of charge across the C–O interatomic surface is nearly the same in the two molecules. The polarization contribution form the oxygen atom is also very similar in the two molecules. The same contribution from the carbon atom is necessarily zero in CO_2, but it is this contribution in CO which is primarily responsible for the very small magnitude of the resultant moment in this system. Both carbon and oxygen are polarized in a direction counter to the direction of charge transfer with the polarization being particularly extreme in the case of the carbon. As noted above and illustrated in Fig. 2, the remaining valence charge density on carbon is strongly polarized into its nonbonded region to give an atom with an unusually large nonbonded radius and nonbonded volume compared to the isolated atom.

The contribution to the dipole resulting from the transfer of charge across an H–X interatomic surface varies in the anticipated manner through the ten-electron series methane to hydrogen fluoride. Contributions both parallel to and perpendicular to the symmetry axis (z) are given for NH_3 and H_2O. There is a small transfer of charge from C to H in methane followed by an increasing degree of charge transfer from H to N, O, and F in the remaining members. The atom-

TABLE III. Atomic and group contributions to molecular dipole moment.[a]

AB	R calc.	$q(A)$	$M(A)$	$M(B)$	μ_p	$\mu_c = q_A(X_A - X_B)$[b]	μ^c Calc.	μ^c Exp.
Li–H	3.0772	+ 0.908	+ 0.004	+ 0.437	+ 0.441	− 2.793	− 2.352	
Li–F	2.9492	+ 0.942	+ 0.022	+ 0.199	+ 0.221	− 2.778	− 2.557	
C–O	2.0963	+ 1.372	+ 1.727	+ 1.078	+ 2.805	− 2.877	− 0.072	+ 0.044
C–O (CO_2)	2.1546	+ 2.718	0.0	+ 0.913	+ 0.913	− 2.928	0.0	
H–C (CH_4)	2.0449	− 0.042	+ 0.072	0.0	+ 0.125	+ 0.086	0.0	
H–N (NH_3)	1.8893	+ 0.359						
z			+ 0.082	− 0.125	+ 0.041	− 0.245	− 0.615	− 0.578
y			− 0.168	0.0	+ 0.168	− 0.632	0.0	
H–O (H_2O)	1.7804	+ 0.638						
z			+ 0.096	+ 0.398	+ 0.295	− 0.679	− 0.768	− 0.730
y			− 0.121	0.0	+ 0.121	− 0.911	0.0	
H–F	1.7033	+ 0.778	+ 0.105	+ 0.417	+ 0.570	− 1.325	− 0.755	− 0.718
H–Cl	2.3970	+ 0.272	+ 0.137	+ 0.054	+ 0.190	− 0.651	− 0.461	− 0.436
H–H	1.3862	0.0	+ 0.104	− 0.104	0.0	0.0	0.0	
N–N	2.0276	0.0	+ 0.618	− 0.618	0.0	0.0	0.0	
F–F	2.5372	0.0	+ 0.266	− 0.266	0.0	0.0	0.0	
H–C in							μ(H–C)	
CH_4	2.0449	− 0.042	+ 0.072	0.0	+ 0.125	+ 0.086	0.211	
C_2H_6	2.0485	− 0.061	+ 0.125	− 0.004	+ 0.121	+ 0.125	0.246	
C_2H_4	2.0298	− 0.017	+ 0.120	+ 0.002	+ 0.122	+ 0.034	0.156	

[a] All quantities in atomic units.
[b] $X_A - X_B$ and $X_H - X_B$ are < 0 in each case and X denotes a component of nuclear position vector.
[c] $\mu < 0$ has the direction $A^+ B^-$; experimental numbers from Ref. 31.

ic polarizations are in a direction opposite to the charge transfer with the sole exception of N in ammonia. In this case the Laplacian of the charge density shows the presence of a pronounced concentration of nonbonded charge lying on the symmetry axis which dominates the atomic moment.[30] In water these charge concentrations are found closer to the oxygen nucleus and lie off the symmetry axis by 70°, while in hydrogen fluoride the nonbonded charge concentration appears as a torus about the internuclear axis. If one partitions the polarization component of X in $H_n X$ among the n H–X bond contributions, the dipole moment of the H–X group has the values + 0.158 for H–C, − 0.506 for H–N, − 0.771 for H–O, and − 0.755 for H–F. The magnitude of μ(H–X) for water exceeds that for hydrogen fluoride because of a large perpendicular component which of course does not contribute to the total moment. The components of the bond dipoles lying along the symmetry axis exhibit the values anticipated on the basis of the relative electronegativities of X, + 0.211, − 0.204, − 0.384, and − 0.755 a.u. for H–C to HF, respectively.

The atomic polarizations reported for the homonuclear diatomic molecules show that each atomic density is polarized away from the neighboring atom. The Laplacian distribution for N_2 shows the presence of a large nonbonded charge concentration on each atom in agreement with the Lewis model for this molecule, thereby accounting for the large dipolar polarization of the N atom.

IV. ATOMIC AND GROUP CONTRIBUTIONS TO THE MOLECULAR POLARIZABILITY

Table IV gives the atomic contributions to the polarizability arising from a change in the atomic polarization $\Delta M(\Omega)$ and their sum $\Delta\mu_p$, for a given linked pair of atoms

wherein the contribution from X in $H_n X$ has been divided by n and correspondingly that for C in CO_2 by 2. The charge transfer contributions $\Delta\mu_c = \Delta q_A (X_A − X_B)$ are, as in the dipole moment tabulation, given for the transfer or charge across a given interatomic surface and are therefore independent of choice of origin. The difference in nuclear coordinates refers to the particular axis in question. The surface contribution to the polarizability for the A–B group cancels upon summing $\Delta\mu_p$ and $\Delta\mu_c$ as do the individual atomic contributions when arranged over both field directions (Table IV). All changes are divided by the field strength to give the contribution to the polarizability tensor.

The polarizability of the ionic molecules parallel and perpendicular to their internuclear axes are quite similar. The contributions parallel the contributions to the dipole moment. Thus the change in polarization of the Li atom is small and smallest in LiF, while the hydrogen atom exhibits exceptionally large changes in its polarization both parallel and perpendicular to the axis. The extent of charge transfer in the unperturbed molecules is greater in LiF than in LiH and the charge distributions of the atoms in LiF are more tightly bound. Thus the transfer of charge induced by the field is considerably smaller in LiF and both atoms are less polarizable than in LiH.

In carbon monoxide, and particularly in carbon dioxide, the polarizability parallel to the axis is significantly greater than that perpendicular to the axis, a result of the large charge transfer contributions to the parallel components in these molecules. The changes in atomic polarizations are greater perpendicular than parallel to the field, but there is a contribution of almost equal size from the transfer of charge across each C–O interatomic surface for the parallel components for these two molecules. These charge transfer contributions are quite similar for the two molecules as are the

TABLE IV. Atomic contributions to molecular polarizability tensor: Charge transfer and polarizations per unit applied field.[a]

A–B	$\Delta M(A)$	$\Delta M(B)$	$\Delta\mu_p$ [c]	$\Delta q_A (X_A − X_B)$	$\alpha_\parallel$ [b] (calc) Atomic sum	Analytical	$\Delta M(A)$	$\Delta M(B)$	$\alpha_\perp^b$ (calc) Atomic sum	Analytical
Li–H	1.42	14.84	16.26	4.71	20.97	20.98	1.17	21.05	22.22	22.07
Li–F	0.33	5.64	5.97	1.09	7.06	7.03	0.27	6.64	6.91	6.94
C–O	4.18	3.55	7.73	6.23	13.96	13.94	6.26	4.70	10.96	10.96
C–O (CO_2)	− 0.16	4.87	4.71	6.56	22.54	22.70	1.29	5.15	11.50	11.60
H–C(CH_4)	1.20	− 2.98	0.46	3.47	15.72	15.71				
H–N (NH_3)										
z	0.80	7.94	3.44	0.69	12.39	12.39				
x,y	0.79	0.70	1.02	3.07	12.27	12.26				
H–O (H_2O)										
z	0.55	4.27	2.69	1.32	8.02	8.01	0.18	7.23	7.59	7.58
y	0.77	1.41	1.47	2.93	8.80	8.80				
H–F	0.77	2.41	3.18	2.32	5.50	5.49	0.05	4.26	4.31	4.30
H–Cl	0.95	6.08	7.03	10.53	17.56	17.57	0.65	14.45	15.10	.15.09
H–H	0.27	0.27	0.54	2.89	6.32	6.33	2.12	2.12	4.24	4.25
N–N	1.63	1.63	3.25	5.49	14.23	14.22	4.70	4.70	9.40	9.39
F–F	1.50	1.50	3.01	4.76	12.53	12.52	2.64	2.64	5.27	5.27

[a] All quantities in atomic units and changes in charge transfer and atomic polarizations are averaged over both field directions.

[b] $\alpha_\parallel$ refers to axial component or a component in plane of nuclei while $\alpha_\perp$ is component perpendicular to axis or plane. The quoted values are from the analytical calculation. They differ slightly from the sum of the atomic contributions because of numerical integration errors.

[c] Polarization contribution per A–B or H–B bond.

changes in polarization of the oxygen atom. The change in the atomic polarization of carbon between the two molecules is, however, quite dramatic. Not only is $\Delta M(C)$ greatly reduced in magnitude in carbon dioxide because of the loss of the diffuse nonbonded charge distribution present on this atom in carbon monoxide, it is of opposite sign for this molecule for the axially applied field. This is an example of a general phenomenon, that an atom internal to the applied field polarizes not in the direction of the field, but in response to the field exerted on it by the polarizations of and transfer of charge between its neighboring atoms. Thus, because of the transfer of electronic charge from one oxygen to the other and the polarization of their electronic charge distributions in the direction of the applied field, the carbon atom experiences an internal field of opposite sign and polarizes accordingly.

The same behavior is found for the carbon atom in methane and as a consequence the contribution to the polarizability from a C–H group is dominated by the charge transfer contribution. The same pattern of charge transfer and atomic polarizations are found to occur in the antisymmetric stretching and bending motions of the methane molecule[12] and the changes in dipole moment which determine the intensities of these vibrational modes in methane have the same origin as the changes in dipole moment that are responsible for its polarizability. Consider the methane molecule to be oriented so that the z axis bisects two HCH angles. In the antisymmetric stretch, two C–H bonds stretch in the positive z direction while the other two shorten. In the antisymmetric bend, the HCH angle for the hydrogens with positive z opens, while that for the two with negative z closes. In both motions the nuclear displacements create a field directed in the negative z direction. There is a transfer of charge from the outwardly to the inwardly displaced hydrogens in both modes, that is, in the direction of the field, the same response that is observed in the presence of the externally applied field. In both modes, the carbon atom polarizes in the direction opposite to the transfer of charge, in the direction of the positive z axis. Thus the carbon atom polarizes in response to the field created by the transfer of charge between the two sets of hydrogen atoms, precisely the behavior observed for the carbon atom in methane when in an externally applied field. In the vibrationally induced changes, the counter polarization of the carbon atom density dominates the charge transfer and polarization contributions from the hydrogens and the negative end of the induced dipole moment is directed in the direction of the outwardly displaced protons.

It is necessary to introduce correlation to recover the observed asymmetry in the parallel and perpendicular components of the polarizability tensor for ammonia,[23] these values being $\alpha_{\parallel} = 16.9$ and $\alpha_{\perp} = 14.2$ a.u. The present results predict the correct relative magnitudes. The changes in polarization of the hydrogens are nearly identical for the two directions, but the change in polarization of the nitrogen atom is over ten times larger along the symmetry axis— along the axis of the nonbonded charge concentration—than it is perpendicular to it. The disparity in the resultant polarization changes is removed by the differing charge transfer contributions which are approximately five times larger for

the transfer of charge between the hydrogens in a perpendicular field than for the transfer across the N–H interatomic surfaces in the parallel field.

A similar relationship is found between the two in-plane components of the polarizability for water as for the parallel and perpendicular components in ammonia. The polarizations of the hydrogens change by similar amounts in both directions, but the oxygen is polarized to a greater extent along the symmetry axis than it is perpendicular to it in the plane of the nuclei. The contribution from the in-plane transfer of charge between the hydrogens is greater than that arising from the transfer of charge across the O–H interatomic surfaces. The polarizability of the water molecule in the direction perpendicular to the plane of the nuclei arises almost totally from the change in the polarization of the oxygen atom, a contribution which almost equals that for the polarization of the N atom in ammonia along the symmetry axis. The ordering of the relative magnitudes of the three calculated contribution to the polarizability agrees with the experimental values which are $\alpha_{xx} = 9.55$, $\alpha_{yy} = 10.31$, and $\alpha_{zz} = 9.91$ a.u.[31] The mean polarizabilities of the H–X groups in the three hydrides are remarkably similar, the values being: C–H 3.93, N–H 4.10, O–H 4.07 a.u.

The contribution to the polarizability in HF arising from the change in polarization of the hydrogen is similar in value to that found in ammonia and water. The axial polarization of F, not unexpectedly, is less than that found for nitrogen or oxygen. As for N and O, the perpendicular polarization of F is greater than that along the axis and the perpendicular moment for F is comparable to the axial moment of oxygen in water, just as the perpendicular component for O is comparable to the axial component for N in ammonia. As in water, nearly the whole of the perpendicular component of the polarizability for the HF molecule comes from the heavy atom.

The relatively large polarizability of HCl comes from the change in polarization of the Cl atom and the large contribution from the transfer of charge across the H–Cl surface. The contribution to the polarizability arising form the perpendicular polarization of the Cl atom is calculated to be slightly greater than the corresponding contribution of the hydrogen atom in LiH.

The largest contribution to the axial polarizabilities of a homonuclear diatomic molecule comes from the transfer of charge across the interatomic surface, an observation made by Stone[6] in his distributed multipole analysis of the polarizability. His choice of a planar partitioning surface at the bond midpoint for N_2 coincides with the interatomic surface for the unperturbed molecule. His calculated contributions to $\bar{\alpha}$ differ from those presented here in spite of his use of a similar basis set, because an arbitrarily defined surface, unlike an interatomic surface, is not displaced by the applied field. Thus his calculated charge transfer between the N atoms of $4.2e$ is close to the change in basin only population for N_2 given in Table II. As anticipated on the basis of the contributions to the dipole moments of these molecules (Table III), the nitrogen atom exhibits the largest change in its axial polarization.

The compounds methane, ethane, and ethylene provide

the opportunity of comparing the field induced charge transfers and polarizations and hence the polarizabilities of the C–H groups in these molecules, as well as the polarizabilities of the methyl and methylene groups. In the unperturbed molecules, there is a transfer of charge from methyl to hydrogen in methane to give $q(H) = -0.042e$, Table III. The charge transfer is zero for methyl in ethane and correspondingly, each hydrogen withdraws more charge from carbon to give $q(H) = -0.061e$. The electronegativity of carbon increases relative to hydrogen as the degree of s character in its bonds to hydrogen increases[12] and the transfer of charge to hydrogen in ethene is reduced so as to yield $q(H) = -0.017e$, Table III. Table III also gives the polarization and charge transfer contributions to the C–H group dipole moment. The polarization contribution is of the same sign as the charge transfer contribution in each case and is very similar for all three molecules. Thus the relative magnitude of the moment is determined by the charge transfer contribution which is a maximum in ethane and a minimum for ethene and the group dipoles follow the same order.

The transfer of charge per unit field from one methyl group to the other in ethane and from one methylene group to the other in ethene induced by a field applied along the C–C axis are the largest of the charge transfers recorded in Table I. Correspondingly, the axial components of the polarizability are largest for these molecules and largest of all for ethene. (See Table V which also gives the atomic and group contributions to the polarizabilities in these molecules.) Listed under the heading $\Delta\mu_c$, for CH_3 and CH_2, are the contributions to the axial polarizabilities arising from the charge transfer between the methyl or methylene groups, a contribution which is largest for ethene. The ordering of the magnitudes of the polarizabilities along the three principal axes are known for ethene and the ordering of the calculated values is in agreement with it. These large polarizabilities are obtained in spite of the carbon atoms in ethane and ethylene being polarized in a direction counter to the direction of the applied field, that is, counter to the direction of charge transfer between the hydrogens for both the parallel and perpendicular components in ethane and for the two in-plane polarizations in ethene. As in methane, the direction of

polarization of the carbon atoms is determined by the internal field resulting from the polarization of, and transfer of, charge between the hydrogen atoms. The carbon atoms in ethylene do polarize in the direction of the applied field when the field is applied perpendicularly to the plane of the nuclei, as such a field does not induce any inter-atomic transfer of charge and the carbons are directly exposed to the field. Since this direction coincides with the major axis of the C–C bond ellipticity,[32] these are the largest of the polarizations observed for a carbon in these molecules.

The atomic and C–H group contributions to the polarizabilities in ethane and ethene are also given in Table V together with the polarizabilities of the methyl and methylene groups. The hydrogens always polarize in the direction of the applied field, as they do in methane (Table IV) and their contributions to the polarizability are quite similar in all three molecules, showing only a relatively small dependence on the direction of the applied field. The polarizations of the carbon atoms always exceed those of the hydrogens and their magnitudes exhibit a greater dependence on field direction. In addition, as pointed out above when the applied field induces a transfer of charge between the hydrogen atoms, the carbon atoms polarize in response to this internally created field rather than to the applied field. Thus the change in polarization contributions to the C–H polarizability components are small or negative except for the out-of-plane contribution in ethene for which there is no inter-atomic charge transfer. The polarizability and charge transfer components add to yield the mean C–H bond polarizabilities recorded in Table V, with ethene exhibiting the largest value, the value for methane being 3.68 a.u.

The principal polarizabilities of the methyl and methylene groups are obtained by summing the C–H contributions and, in the case of zz components, adding the contribution for the transfer of charge across the C–C interatomic surface, contributions which are equally divided between the groups. It is these contributions which make the polarizability components along the C–C bond the largest in each of these molecules and largest for ethene. The mean polarizabilities of the methyl and methylene groups are quite similar, a result anticipated on the basis of the similar volumes for the

TABLE V. Atomic contributions to polarizability tensor in ethane and ethene: Charge transfer and polarization contributions per unit applied field.[a]

Molecule and component	$\Delta M(H)$	$\Delta M(C)$	$\Delta\mu_p$(C–H)	$\Delta\mu_c$(C–H)	α_{ii}(C–H)	values for CH_1 or CH_2 $\Delta\mu_c$	α_{ii}	α_{ii} (calc) Atomic sum	Analytical	α_{ii}(exp)[b]
C_2H_6										
$\parallel$	1.55	−5.15	−0.16	1.70	1.54	9.87	14.49	28.98	29.06	
$\perp$	1.07	−3.28	−0.02	4.31	4.29	-	12.87	25.75	25.77	
				$\bar\alpha$(C–H) $= 3.37$		$\bar\alpha(CH_3)^c = 13.43$		$\bar\alpha = 26.87$		30.4
C_2H_4										
zz	1.15	−4.39	−1.04	3.83	2.79	12.10	17.68	35.37	35.38	36.4
xx	0.73	−3.35	−0.94	6.89	5.95	-	11.90	23.80	23.78	26.0
yy	1.25	+8.03	+5.27	0.0	5.27	-	10.53	21.06	21.02	22.9
				$\bar\alpha$(C–H) $= 4.67$		$\bar\alpha(CH_2) = 13.37$		$\bar\alpha = 26.73$		28.4

[a] All quantities are in atomic units and changes in charge transfer and atomic polarization are averaged over both field directions.
[b] From Ref. 31.
[c] In methane, $\bar\alpha(CH_3) = 14.5$ a.u.

two groups. As in methane, the changes in the atomic contributions to the molecular dipole moment of ethene as caused by vibrational displacements of the nuclei,[12] parallel the atomic contributions to the polarizability for corresponding fields. The B_{3u} antisymmetric stretching and bending modes result in a transfer of charge between the methylene groups across the C–C internuclear axis and in each case the centroid of the charge distribution of each carbon atom is displaced in the opposite direction. In the B_{2u} in-plane antisymmetric stretch, charge is transferred between the hydrogen atoms in a direction perpendicular to the internuclear axis and again the carbon atoms polarize in the direction opposite to this transfer. In the B_{1u} out-of-plane bending mode, the carbon atoms polarize in a direction counter to the displacement of the hydrogens in the direction of the field, as they do in response to an external field applied in this direction. Their change in polarization is the largest single contribution to the change in dipole moment for this motion of the nuclei.

V. CONCLUSIONS

A molecular polarizability is determined by the polarization of the atoms and by the transfer of charge between them, as caused by an externally applied field. The transfer of charge across an interatomic surface can make the largest single contribution to the polarizability, as is observed for the homonuclear diatomics and for ethane and ethene. The same contribution is smallest for the ionic system LiF where both atomic charge distributions are tightly bound. The charge transfer contribution to the polarizability increases with the distance over which the charge is transferred, being largest in the present series of molecules for the charge transferred between the two sets of equivalent hydrogens in ethane and ethene. This contribution is expected to increase with chain length for the axial component of the polarizability in the normal hydrocarbons. This point is further discussed and illustrated in a companion paper[33] on the polarizabilities of the normal hydrocarbons. The same study provides further and even more striking examples of another important property of the atomic contributions to a molecular polarizability; that atoms internal to a molecule polarize in a direction counter to the applied field. Thus the effect noted in methane, ethane, and ethene, that the carbon atoms polarize against the applied field and respond instead to the field exerted on them by the perturbed hydrogen distributions, is found in propane and butane as well. In these two molecules the hydrogen atoms form an outer sheath of charge density which polarizes with the field, while the chain of carbon atoms form an inner tube of oppositely polarized charge density. A related observation is that the same polarizations and transfers of charge that are induced by an externally applied field, are found for the fields generated within the molecule by the displacement of its nuclei. There is clearly an intimate relationship between the atomic contributions to the polarizability and their contributions to the vibrationally induced changes in dipole moment which determine the intensities of infrared vibrational modes.

The linear correspondence which exists between the mean polarizability of a molecule and its volume, as determined by an outer envelope of the charge density within the theory of atoms in molecules, was pointed out previously[8] and further examples are given here for a wider range of atomic interactions. The existence of a single correlation for all interactions (with the sole exception of LiH) is striking, as exemplified by the isoelectronic pair of molecules N_2 and CO. Both have similar molecular volumes 233 and 244 a.u., respectively, and similar mean polarizabilities of 12 and 13 a.u., in the same order. The atomic polarizations, which are the sole contributions to the perpendicular moments from C and O average to 5.5 a.u. compared to a value of 4.7 a.u. for N. Most striking is the similarity in their parallel components of 14.0 and 14.2 a.u. for CO and N_2 respectively, in spite of the quite different charge transfer and polarization contributions (Table IV).

The theory of atoms in molecules demonstrates that one can rigorously define a group contribution to a molecular polarizability. This demonstration, together with the ability of the theory to assign volumes to individual atoms and functional groups, not only places the correlations between molecular polarizability and volume on a firm theoretical basis but makes possible the assignment of a mean polarizability to a molecule through a knowledge of the volumes of its constituent groups, quantities which are characteristic for a given functional group and which in addition, are readily calculated and tabulated. The volumes of the methyl and methylene groups of the hydrocarbons for example, are transferable and a corresponding transferability of the polarizabilities of these groups is the subject of the companion paper.[33]

[1] R. J. W. Le Fevre, Adv. Phys. Org. Chem. 3, 1 (1965).
[2] M. V. Wolkenstein, L. A. Gribov, M. A. Eliashevich, and B. I. Stepanov, The Vibrations of Molecules (Nauka, Moscow, 1972).
[3] R. E. Hester, in Molecular Spectroscopy, edited by R. F. Barrow, D. A. Long, and D. J. Millen (Chemical Society, London, 1974), Vol. 2, pp. 439–465; M. Gusoni, S. Abbate, and G. Zerbi, in Vibrational Spectroscopy–Modern Trends, edited by A. J. Barnes and W. J. Orville-Thomas (Elsevier, Amsterdam, 1977), pp. 205–222; M. Gusoni, in Advances in Infrared and Raman Spectroscopy, edited by R. J. H. Clark and R. E. Hester (Heyden, London, 1980), Vol. 6, pp. 61–126.
[4] Vibrational Intensities in Infrared and Raman Spectroscopy, edited by W. B. Person and G. Zerbi (Elsevier, Amsterdam, 1982).
[5] J. Applequist, Acc. Chem. Res. 10, 79 (1977).
[6] A. J. Stone, Mol. Phys. 56, 1065 (1985).
[7] A. Dalgarno, Adv. Phys. 11, 281 (1962).
[8] K. M. Gough, J. Chem. Phys. 91, 2424 (1989).
[9] R. F. W. Bader and T. T. Nguyen-Dang, Adv. Quantum Chem. 14, 63 (1981).
[10] R. F. W. Bader, Atoms in Molecules: A Quantum Theory (Oxford University Press, Oxford, 1990).
[11] R. F. W. Bader, M. T. Carroll, J. R. Cheeseman, and C. Chang, J. Am. Chem. Soc. 109, 7968 (1987).
[12] R. F. W. Bader, A. Larouche, C. Gatti, M. T. Carroll, P. J. MacDougall, and K. B. Wiberg, J. Chem. Phys. 87, 1142 (1987).
[13] R. F. W. Bader, J. Pure Appl. Chem. 60, 145 (1988).
[14] R. F. W. Bader, J. Chem. Phys. 91, 6989 (1989).
[15] C. J. Jameson and A. D. Buckingham, J. Chem. Phys. 73, 5684 (1980).
[16] GAUSSIAN 88, M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1988.
[17] (a) T. H. Dunning, J. Chem. Phys. 53, 2823 (1970); 55, 716 (1971); (b) S. Huzinaga, Gaussian Basis Sets for Molecular Calculations (Elsevier,

Amsterdam, 1984). The basis set for Cl is the Dunning–Hay [6s4p] contraction of Huzinaga's [11s7p] set with Huzinaga's set of two 3d polarization functions; (c) T. H. Dunning and P. J. Hay, *Methods of Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1977); (d) J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, J. Mol. Struct. (THEOCHEM) **89**, 185 (1982).

[18] H. J. Werner and W. Meyer, Mol. Phys. **31**, 855 (1976).

[19] R. D. Amos, Chem. Phys. Lett. **113**, 19 (1985).

[20] D. M. Bishop and G. J. Maroulis, J. Chem. Phys. **94**, 43 (1985).

[21] B. O. Roos and A. J. Sadlej, J. Chem. Phys. **76**, 5444 (1982).

[22] S. Y. Liu and C. E. Dykstra, J. Phys. Chem. **91**, 1749 (1987).

[23] M. A. Spackman, J. Chem. Phys. **93**, 7594 (1989).

[24] P. C. Hariharan and J. A. Pople, Chem. Phys. Lett. **66**, 217 (1972); W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972); J. S. Binkley and J. A. Pople, *ibid*. **66**, 879 (1977); M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, *ibid*. **77**, 3654 (1982).

[25] R. F. W. Bader and H. Essen, J. Chem. Phys. **80**, 1943 (1984). The fluorine molecule with $\nabla^2 \rho_b$ just positive, is borderline with the intermediate interactions.

[26] R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys. **46**, 3341 (1967).

[27] T. Slee, A. Larouche, and R. F. W. Bader, J. Phys. Chem. **92**, 6219 (1988).

[28] J. A. Pople, R. Krishnan, H. B. Schelgel, and J. S. Binkley, Int. J. Quantum Chem. Symp. **13**, 225 (1979).

[29] The presence of a substantial positive charge on C in CO_2 can be used to account for the ring structure found for the $HBr–CO_2$ complex wherein Br is bonded to C. S. W. Sharpe, Y. P. Zeng, and C. Wittig, and R. A. Beaudet, J. Chem. Phys. **92**, 943 (1990).

[30] R. F. W. Bader, P. J. MacDougall, and C. D. H. Lau, J. Am. Chem. Soc. **106**, 1594 (1984).

[31] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Oxford University Press, Oxford, 1984), Vol. 1.

[32] R. F. W. Bader, T. S. Slee, D. Cremer, and E. Kraka, J. Am. Chem. Soc. **105**, 5061 (1983).

[33] K. M. Gough, K. E. Laidig, and R. F. W. Bader (to be submitted).