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Where Do the Forces in Molecules Come from? A Density Functional Study of N_2 and HCl

J. Autschbach[†] **and W. H. E. Schwarz***

Theoretical Chemistry, University of Siegen, D-57068 Siegen, Germany

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Though chemical forces in molecules have been of considerable interest for decades, the question of the origin of such forces concerning different spatial regions in a molecule is still open to discussion. In this paper we investigate chemical forces by a density functional study of two molecules, N_2 and HCl. On the one hand, we find that the quantitative details of slight polarizations of the electronic densities in the atomic core regions yield major contributions to the forces, and this is responsible for the difficulties in calculating reliable forces from approximate electron densities. On the other hand, the qualitative topology of the electron density in the valence region is not at all unimportant for electrostatic forces, and this is responsible for the possibility of a qualitative chemical interpretation of electrostatic binding.

1. Introduction

1.1. Electron Density and Force. The electron density $\rho(\mathbf{r})$ and its topological features can be employed as a principal basis of understanding chemical bonding. Namely, ρ determines (i) the total energy E and thereby the bond energy BE and (ii) the binding forces F. Here we follow the convention that bonding refers to energy and binding refers to (electrostatic) force. The theoretical justification of point (i) had formally not been proven before 1965 by Hohenberg and Kohn,[1] and it is still an unsolved problem: *how* to determine the energy of atoms and molecules solely from the electron density. Concerning point (ii), it has already been shown in the very begining years of quantum mechanics by Hellmann (in 1933!;[2] for later references, see refs 3 and 4) how the binding forces can be computed directly from the electron density. The well-known so-called Hellmann−Feynman formula reads

$$\mathbf{F}_A = -\frac{\partial E}{\partial \mathbf{R}_A} = \int d\mathbf{r}\, \hat{\boldsymbol{F}}_A \rho(\mathbf{r}) \tag{1}$$

where the vector $\mathbf{F}_A$ is the force on nucleus A at position $\mathbf{R}_A$, $N_{el}\rho(\mathbf{r})$ is the total electronic charge density, with normalization $\int d\mathbf{r}\ \rho(\mathbf{r}) = 1$, and

$$\hat{\boldsymbol{F}}_A = \hat{\boldsymbol{F}}_A^{el} + \hat{\boldsymbol{F}}_A^{nuc} = -N_{el} Z_A \frac{\mathbf{r}_A}{r_A^3} + Z_A \sum_{B \neq A} Z_B \frac{\mathbf{R}_{AB}}{R_{AB}^3} \tag{2}$$

is the Hellmann−Feynman force vector operator corresponding to the molecular Hamiltonian. $\mathbf{r}_A$ is the distance vector of an electron from nucleus A with nuclear charge Z_A, r_A is its absolute value, and $\mathbf{R}_{AB}$ is the distance vector between the two nuclei A and B. Atomic units ($m_e = 1$, $\hbar = 1$, $4\pi\epsilon_0 = 1$) are used throughout this paper unless stated otherwise. It is important to note that the derivation of eq 1 is, in the most simple case, based on the assumption that $\rho(\mathbf{r})$ is the *exact* electron density of the molecule, computed from the *exact* N_{el}-electron wavefunction by

$$\rho(\mathbf{r}) = \int d\mathbf{r}'\ \psi^* \psi \tag{3}$$

Here, $\int d\mathbf{r}'$ means integration over all electronic spin coordinates and all spatial coordinates but one.

1.2. Different Expressions of the Force. The validity of the Hellmann−Feynman force theorem (and its generalizations) can also be proven for (exact or specially optimized densities of) several model systems such as Hartree−Fock or Xα.[5,6] The crucial point is that the force theorem does not hold in general for approximate densities, especially not in the standard quantum chemical case, where basis functions are centered on the moving nuclei. It is well-known that the errors of the force introduced by the "fixed-center basis set approximation" can be enormously large even for good quality standard basis sets. As a consequence, forces in molecules (for instance needed during geometry optimizations) are usually computed as the exact gradient of the respective approximate energy expectation value $\langle E \rangle = \langle \psi | \hat{H} | \psi \rangle$, which then includes all terms that would sum up to zero upon integration if ψ were the exact eigenfunction of $\hat{H}$.

This has lead to a somewhat paradoxical situation. On the one hand, eq 1 is conceptually quite simple since it connects the features of the electron density in real space directly with the chemical forces. From a computational as well as from an experimental (i.e., density measurement) point of view, it is very attractive to use eq 1 for the interpretation of chemical binding, and numerous examples of such interpretations can be found in the literature (see, e.g., ref 7). On the other hand it is computationally demanding and, with present-day technology, practically impossible by experimental methods to obtain the electron density with a high enough accuracy that the application of eq 1 would result in reasonably accurate forces, or at least in forces of the correct sign. Conversely, the requirement that the force vanishes at internuclear equilibrium can be used to improve the experimental polarization of the core density![8] Nevertheless, such approximate electron densities are usually accurate enough to reproduce a reasonable description of the molecule, e.g., appropriate deformation densities ($\Delta\rho$), density Laplacians ($\nabla^2\rho$), or energy density functionals ($\epsilon(\rho)$).

The qualitative interpretations of chemical binding with the help of eq 1 are usually based on specific topological features

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* Corresponding author: e-mail schwarz@chemie.uni-siegen.de.

[†] Present address: Theoretical Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta T2N 1N4, Canada. E-mail: jochen@cobalt78.chem.ucalgary.ca.

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of the electron density in the valence and bond regions of the molecules, which are often already qualitatively well represented by moderately sized basis sets. Yet the computation of the forces using eq 1 often leads to totally wrong results. It is our aim here to discuss this curious situation and to answer the question about the spatial origin of the forces.

The following aspect is important in this context. In order to explain the "physical nature of a chemical phenomenon", the mathematical formula of the respective physical observable should be made transparent so that the sign and order of magnitude of the numerical value become obvious. In quantum mechanics, those formulas consist of integrals over the whole space. A great many replacements and transformations, including gauge transformations of the basic fields as well as of the chemical forces, and integral transformations and partial integrations, are possible to modify the respective mathematical expression. Accordingly, the explanation of the physical nature of a phenomenon can be cast into many different, often paradoxical, forms.

1.3. Outline. The paper is organized as follows: In section 2 the gauge freedom of the force is reviewed. In section 3 the general formulas of force density and energy gradient density functions are discussed. Section 4 considers suitable expressions for the nuclear repulsion force density. After a short section 5 on computational details, spatial contributions to the forces in N_2 and HCl molecules are analyzed in section 6. Section 7 contains some final conclusions.

2. Internal Coordinates and Gauge of the Force

From now on we will consider a diatomic molecule A−B along coordinate axis x, i.e., $\mathbf{R}_A = (X_A,0,0)$ and $\mathbf{R}_B = (X_B,0,0)$, cf. Figure 1. There are six positional variables, while the molecular bonding energy only depends on a single variable, the internuclear distance $R = |\mathbf{R}_{AB}|$. Because of the σ_v mirror symmetry of the molecular electron density, E depends on X_A and X_B only, while $\partial E/\partial Y_A = 0$ etc. Introducing a translational transformation (compare also Silberbach[9]) with gauge parameter η

$$X_A = S - \frac{1+\eta}{2}R \tag{4a}$$

$$X_B = S + \frac{1-\eta}{2}R \tag{4b}$$

we find for the nonvanishing component of $\mathbf{F}_{AB} = (F(R),0,0)$ in the direction $\mathbf{R}_{AB}$, as the physical invariant, which can be split up arbitrarily into two contributions:

$$\begin{aligned} F(R) &= -\frac{\partial E(R)}{\partial R} \\ &= -\left(\frac{\partial E}{\partial X_A}\right)_{X_B}\frac{\partial X_A}{\partial R} - \left(\frac{\partial E}{\partial X_B}\right)_{X_A}\frac{\partial X_B}{\partial R} \\ &= F_A\frac{1+\eta}{2} + F_B\frac{1-\eta}{2} = \frac{F_A+F_B}{2} + \eta\frac{F_A-F_B}{2} \end{aligned} \tag{5}$$

S in eq 4 has the meaning of an "η-weighted" center of the molecule, where η specifies the relative shifts of the two nuclei. $\eta = 0$ means that the geometrical center of the nuclei remains fixed upon variation of R, i.e., both nuclei are shifted by 0.5 dR toward each other when determining the energy gradient or force. Berlin[10] had chosen this η-value implicitly without any discussion, and Hinze[11] strongly advocated for this special choice as the only reasonable one. $\eta = \pm 1$ means that only one of the two nuclei is shifted. Other special choices are fixing the center of mass (CM) or charge (CC) of the nuclei:

$$\eta^{CM} = \frac{M_B - M_A}{M_B + M_A} \tag{6a}$$

$$\eta^{CC} = \frac{Z_B - Z_A}{Z_B + Z_A} \tag{6b}$$

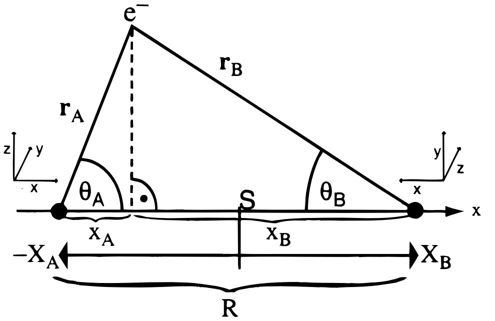
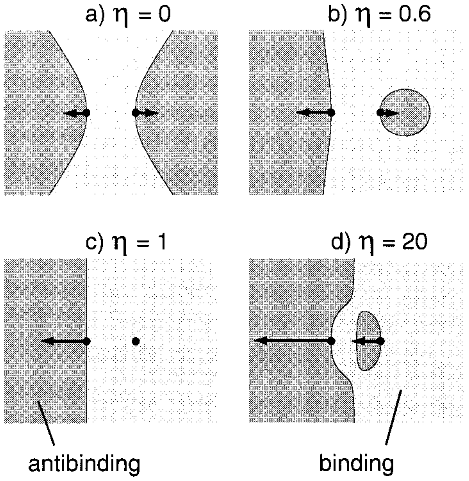


Figure 1. Coordinates of a diatomic molecule A−B oriented along the x-axis. The nuclear positions on the axis are marked by dots. Note the directions of the x-coordinates, which are consistent with the signs in eqs 4−7; they ensure $F_A^{el} = +F_B^{el}$.


a) $\eta = 0$ b) $\eta = 0.6$

c) $\eta = 1$ d) $\eta = 20$

Figure 2. Gauge dependent binding and antibinding regions in a diatomic molecule. (The η-values refer to the homonuclear case $Z_A = Z_B$.) A negative sign of F^{el}, eq 7, corresponding to binding forces, is indicated by light, and a positive sign (antibinding forces) by dark shading. The arrows symbolize the relative weight and direction of the shifts of each nucleus. $\eta = 0$ means equal translations in opposite directions, $\eta = \pm 1$ means that only one nucleus is shifted by twice the amount.

Koga et al.[12] and recently Ishida and Ohno[13] have strongly advocated for restricting oneself to the η^{CM} choice, which corresponds to the nuclear motions of a molecule vibrating in free space. They also mentioned that for non-hydrogenic nuclei with $M_A \approx 2Z_A$, $\eta^{CM} \approx \eta^{CC}$, while for hydrides the two choices of η are quite different, though both are not too different from unity. Since the forces originate in the charges of the particles, η^{CC} may also be preferable in some discussions. η^{CC} corresponds to the symmetric Berlin diagram (a) in Figure 2. For specific purposes it may be more useful to investigate F_A or F_B individually, i.e., $\eta = \pm 1$.

The electronic part of the force operator, eq 2, corresponding to eq 5 and Figure 1, reads

$$\hat{F}^{\mathrm{el}} = -N_{\mathrm{el}}\left[\frac{1+\eta}{2}Z_{\mathrm{A}}\frac{\cos\theta_{\mathrm{A}}}{r_{\mathrm{A}}^2} + \frac{1-\eta}{2}Z_{\mathrm{B}}\frac{\cos\theta_{\mathrm{B}}}{r_{\mathrm{B}}^2}\right] \qquad (7)$$

For the nuclear repulsion force it is desirable to introduce an operator that similarly depends on the gauge through η and is split up into two terms in such a way that one obtains a chemically sensible classical force picture at large distances (see section 4).

As pointed out by Berlin,[10] $\hat{F}^{\mathrm{el}}$ is a real function in three-dimensional space, and since the electron density $\rho(\mathbf{r})$ is everywhere positive, the sign of $\hat{F}^{\mathrm{el}}$ defines binding and antibinding regions in a molecule in an η-dependent manner. Figure 2 shows different "Berlin diagrams". The gauge freedom motivated Silberbach[9] to completely reject Berlin's concept of binding and antibinding regions in a molecule, since they are not uniquely defined corresponding to the Galilei−Newton arbitrariness of coordinate choice.

3. The Force and the Energy Gradient

3.1. Discussion of the Force Expression. The total energy of a molecule (in the Born−Oppenheimer approximation, neglecting the kinetic energy of the nuclei) reads

$$E = \langle\psi|\hat{H}|\psi\rangle = \langle\hat{T}_e\rangle + \langle\hat{V}_{Ne}\rangle + \langle\hat{V}_{ee}\rangle + \langle\hat{V}_{NN}\rangle \qquad (8)$$

For ψ exactly fulfilling $(\hat{H} - E)\psi = 0$, one obtains eqs 1 and 2, i.e.,

$$F = -\left\langle\psi\left|\frac{\partial}{\partial R}[\hat{V}_{Ne} + \hat{V}_{NN}]\right|\psi\right\rangle \qquad (9)$$

while the sum of the remaining terms vanishes,

$$\frac{\partial\langle\hat{T}_e\rangle}{\partial R} + \left\langle\hat{V}_{Ne}\left|\frac{\partial\rho}{\partial R}\right.\right\rangle + \frac{\partial\langle\hat{V}_{ee}\rangle}{\partial R} + \left\langle\hat{V}_{NN}\left|\frac{\partial\rho}{\partial R}\right.\right\rangle = 0 \qquad (10)$$

Since this does, of course, not mean the vanishing of any individual term in eq 10, one must, and should not, support arguments in favor of the apparently vanishing role of the kinetic electron energy in chemical binding. It is just the following type of replacement of kinetic energy by potential energy terms through inserting the Schrödinger equation, i.e.

$$\langle\phi_b|\hat{T}_e - E_a|\phi_a\rangle = -\langle\phi_b|\hat{V}_a|\phi_a\rangle \qquad (11)$$

which, since the early times of quantum chemistry,[14,15] evoked this argumentation. The force theorem suggests only illusorily that the binding force is essentially electrostatic. The convenient result of a purely electrostatic force expression is obtained from the knowledge that, upon electronic integration of the nuclear gradient of the *exact* quantum chemical electronic density, the *sum* of eq 10 will vanish *exactly*.

Hence there exist conceptionally different notions of different physical pictures: on the one hand, there is the seemingly purely electrostatic force, on the other hand, there is the complete gradient of the molecular bonding energy, containing derivatives of each individual energy term of the Hamiltonian, including the contribution from $\langle\hat{T}_e\rangle$. Furthermore the "energy gradient function" in space, $\partial(\psi^*\hat{H}\psi)/\partial R$, has no similarity at all to the "force function", $\psi^*(\partial\hat{H}/\partial R)\psi$, see below. Accordingly, the energy gradient will provide a completely different spatial picture than the force. To avoid ambiguities, we note again that upon integration both quantities give the same numerical result for the total force, but the contributions of $\partial(\psi^*\hat{H}\psi)/\partial R$ and of $\psi^*(\partial\hat{H}/\partial R)\psi$ come from different regions in space.

3.2. Expressions for the Energy Gradient. We will now investigate *energy gradient* density functions which, after integration over 3D space, yield the energy gradient or force value. This is the first-order perturbation energy $E^{(1)}$ with respect to δ, where the perturbation δ is the *negative* change of internuclear distance. For convenience, δ is chosen here so that the signs correspond to $E^{(1)} = F = -\partial E/\partial R$. The superscripts in parentheses denote the perturbation order with respect to δ. Multiplication by ψ^* of the Schrödinger equation $\hat{H}\psi = \psi E$ leads, after integration, to

$$E\rho(\mathbf{r}) = \int \mathrm{d}\mathbf{r}'\ \psi^*\hat{H}\psi \qquad (12)$$

Cf. eq 3 for the definition of $\int\mathrm{d}\mathbf{r}'$. The energy density function $\psi^*\hat{H}\psi$ of a system is, pointwise, just the electron density multiplied by E. The first-order perturbation of eq 12 is

$$\textbf{(A)}\ E^{(1)}\rho^{(0)}(\mathbf{r}) + E^{(0)}\rho^{(1)}(\mathbf{r}) = \int\mathrm{d}\mathbf{r}'[\psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} + \psi^{(1)*}\hat{H}^{(0)}\psi^{(0)} + \psi^{(0)*}\hat{H}^{(0)}\psi^{(1)}] \qquad (13)$$

where $\hat{H}^{(1)} = \partial\hat{H}/\partial\delta$, $\rho^{(1)} = \partial\rho/\partial\delta$ etc. We assume $\langle\psi^{(0)}|\psi^{(1)}\rangle = 0$. From the first-order perturbation equation,

$$\hat{H}^{(0)}\psi^{(1)} + \hat{H}^{(1)}\psi^{(0)} = E^{(1)}\psi^{(0)} + E^{(0)}\psi^{(1)} \qquad (14)$$

it follows that the function $\psi^{(0)*}\hat{H}^{(1)}\psi^{(0)}$ on the right-hand side of eq 13, i.e., the force density, strongly diverging at the nuclei according to eq 7, is *pointwise* cancelled by terms contained in the function $\psi^{(0)*}\hat{H}^{(0)}\psi^{(1)}$. Thereby the function on the left-hand side of eq 13 results, which is much smoother at the nuclei.

Alternatively, one may multiply eq 14 by $\psi^{(0)*}$ and integrate as in eq 3 to obtain

$$\textbf{(B)}\ E^{(1)}\rho^{(0)}(\mathbf{r}) + {}^1/_2E^{(0)}\rho^{(1)}(\mathbf{r}) = \int\mathrm{d}\mathbf{r}'[\psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} + \psi^{(0)*}\hat{H}^{(0)}\psi^{(1)}] \qquad (15)$$

We see from eqs 13 and 15 that the energy gradient density function of the molecule is given by two terms. The first one is its electron density $\rho^{(0)}(\mathbf{r})$ multiplied by $E^{(1)}$, which yields the gradient or force *value* $E^{(1)} = F = -\partial E/\partial R$ upon integration. It is superimposed by another function $\rho^{(1)}(\mathbf{r}) = -\partial\rho/\partial R$, multiplied by some arbitrary factor, for instance $E^{(0)}$ in eq 13, or alternatively $E^{(0)}/2$ in eq 15. Upon integration it does not contribute to the numerical expectation value of the force, since $\rho^{(1)}$ integrates up to zero.

3.3. Relation of Different Expressions. Exploiting, upon integration of eq 13 or 15, the hermitian property of $\hat{H}^{(0)}$ and the relation $(H^{(0)} - E^{(0)})\psi^{(0)} = 0$ for exact $\psi^{(0)}$, the *force* is obtained as

$$F = E^{(1)} = \langle\psi^{(0)}|\hat{H}^{(1)}|\psi^{(0)}\rangle \qquad (16)$$

The last two terms on the right-hand side of eq 13, or the last term on the right-hand side of eq 15, vanish *after* integration; see eq 10. Deleting a part or all of these terms, we go from eq 13 to eq 15 to eq 17,

$$\textbf{(C)}\qquad \hat{F}\rho(\mathbf{r}) = \int\mathrm{d}\mathbf{r}'\psi^{(0)*}\hat{H}^{(1)}\psi^{(0)} \qquad (17)$$

This drastically changes the integrand function without changing the integral value in the case of an exact ψ (except its error sensitivity), and one obtains the force density from the energy gradient density. At the nuclear equilibrium distance, where $E^{(1)} = 0$, i.e., where the nuclear and electronic forces are at equilibrium and the total force or energy gradient vanish, the topology of the energy gradient density, eq 13, is solely determined by the topology of $\rho^{(1)} = -\partial\rho/\partial R$. The force density, eq 17, depicts a completely different picuture of binding in terms of electrostatic forces, involving a $1/r^2$ factor. The difference in these two equivalent pictures reflects again the hidden, but nevertheless important, role of the kinetic energy for chemical bonding.

Noting that the first-order equation (14) means that

$$\int \mathrm{d}\mathbf{r}'\ \psi^{(0)*}\hat{H}\psi^{(1)} = -\frac{\partial E}{\partial R}\rho + \hat{F}\rho - \frac{E}{2}\frac{\partial \rho}{\partial R} \qquad (18)$$

a more general expression for the density function $f(\mathbf{r})$, yielding the force or gradient value upon integration, reads

$$(\mathbf{D})\ f_{\lambda,\mu,\eta}(\mathbf{r}) = \lambda\hat{F}_{\eta}(\mathbf{r})\rho(\mathbf{r}) - (1-\lambda)\frac{\partial E}{\partial R}\rho(\mathbf{r}) - \mu E\frac{\partial \rho(\mathbf{r})}{\partial R} \qquad (19)$$

where (λ; μ) and η are arbitrary parameters. The special cases "expectation value" (**A**:13), "first-order equation" (**B**:15), and "force expression" (**C**:17) are contained in the general force and energy gradient density expression (**D**:19). The three special forms (13), (15), and (17) are represented by (λ; μ) = (0; 1), (0; $^1/_2$), and (1; 0), respectively.

4. Choice of Nuclear Repulsion and Promolecular Forces

The electron density ρ of a molecule can be represented as the superposition of (i) densities of the independent spherical atoms ρ_A (the so-called *promolecular density* $\rho^{\rm pro}$) and (ii) a molecular *density deformation* $\Delta\rho$:

$$N_{\rm el}\rho = \sum_{\rm A} N_{\rm A}\rho_{\rm A} + \Delta\rho = \rho^{\rm pro} + \Delta\rho \qquad (20)$$

where $\int \mathrm{d}\mathbf{r}\ \rho_{\rm A} = 1$, $\int \mathrm{d}\mathbf{r}\ \Delta\rho = 0$, and $N_{\rm el} = N_{\rm A} + N_{\rm B}$. The electronic part of the force, $F^{\rm el}$, and the nuclear repulsion force, $F^{\rm nuc}$, being of opposite sign, can be several orders of magnitude larger than the total force $F = F^{\rm el} + F^{\rm nuc}$, especially near the equilibrium internuclear distance. The major part of the electronic binding force $F_{\rm A}^{\rm el}$ on nucleus A is trivially due to the shielding of the repulsion of nuclear charge $Z_{\rm B}$ by the promolecular electron density, canceling the nuclear repulsion force almost totally. It is desirable to eliminate these two huge contributions of different sign from the discussion of the total binding force. This is achieved by introducing an η-gauge also into the nuclear repulsion force so that the promolecular contributions from both atoms to both $F^{\rm el}$ and $F^{\rm nuc}$ approximately cancel each other for any choice of η. From the Schrödinger equation, the gauge-free nuclear repulsion force density is initially obtained as

$$\hat{F}^{\rm nuc}\rho(\mathbf{r}) = \frac{Z_{\rm A}Z_{\rm B}}{R_{\rm AB}^2}\rho(\mathbf{r}) \qquad (21)$$

A suitable choice for an η-gauge of $F^{\rm nuc}$ can be achieved through $\rho \rightarrow \tilde{\rho}_\eta$

$$\tilde{\rho}_\eta = \frac{1+\eta}{2}\tilde{\rho}_{\rm B} + \frac{1-\eta}{2}\tilde{\rho}_{\rm A} \qquad (22)$$

where $\tilde{\rho}_{\rm A}$ and $\tilde{\rho}_{\rm B}$ are the densities of the deformed "atoms in molecules", i.e., $N_{\rm el}\rho = N_{\rm A}\tilde{\rho}_{\rm A} + N_{\rm B}\tilde{\rho}_{\rm B}$. (Concerning another decomposition of $\hat{F}^{\rm nuc}$, see ref 13). The most simple possibility of choosing $\tilde{\rho}_{\rm A}$, $\tilde{\rho}_{\rm B}$ is to approximate these functions by the promolecular independent atom densities $\rho_{\rm A}$, $\rho_{\rm B}$, thereby keeping the exact normalization and the value of the integral:

$$F^{\rm nuc} = F^{\rm nuc,pro} = \int \mathrm{d}\mathbf{r}\ \frac{Z_{\rm A}Z_{\rm B}}{R_{\rm AB}^2}\left(\frac{1+\eta}{2}\rho_{\rm B} + \frac{1-\eta}{2}\rho_{\rm A}\right) \qquad (23)$$

There are two points justifying such an approach:

(i) As mentioned above, the promolecular electronic force,

$$F^{\rm el,pro} = \int \mathrm{d}\mathbf{r}\cdot\frac{\hat{F}^{\rm el}}{N_{\rm el}}\cdot(N_{\rm A}\rho_{\rm A} + N_{\rm B}\rho_{\rm B}) \qquad (24)$$

never completely compensates the nuclear repulsion force $Z_{\rm A}Z_{\rm B}/R^2$. This means, the essential molecular binding effects come from the electronic force of the molecular deformation density $F^{\Delta\rho}$:

$$F = F^{\rm el,pro} + F^{\rm nuc,pro} + F^{\Delta\rho} \qquad (25)$$

with

$$F^{\Delta\rho} = \int \mathrm{d}\mathbf{r}\cdot\frac{\hat{F}^{\rm el}}{N_{\rm el}}\cdot\Delta\rho \qquad (26)$$

From this point of view, which has extensively been discussed in the literature,[16,17] the nuclear repulsion force is considered as a promolecular property.

(ii) At large internuclear distances, the nuclear repulsion force $F_{\rm A}^{\rm nuc}$ is almost completely compensated by $F_{\rm A}^{\rm el}$ through the electron density contributions $\rho_{\rm B}$ around nucleus B, and vice versa. Our choice of weighting the nuclear repulsion force at the one nucleus with the atomic electron density around the other nucleus ensures that at large internuclear distances the spatial contributions to the electronic force are compensated by the contributions to the nuclear repulsion force in the *same regions of space*.

5. Definitions and Computational Details

All computations were performed with the Amsterdam Density Functional (ADF) program[18,19] using the Vosko–Wilk–Nusair (VWN) functional[20] and the Becke 88 + Perdew 86 gradient corrections.[21,22] As already mentioned above, approximate electron densities in general do not fulfil the force theorem. To overcome this problem, comparatively large multi-ζ polarized Slater type basis sets together with a highly accurate numerical integration technique[23,24] were applied. In this context the polarization of the core density plays a crucial role. Therefore sufficient p, d, and f polarization functions for both the valence *and* the core shells were added. Compare also refs 13 and 25.

The polarization of the core densities, $\Delta^{\rm pol}\rho$, was analyzed by two methods: either by accurate numerical integration of the basis representation or by a partial wave decomposition (i.e., the *density* is decomposed into s, p, d, f, ... components around one of the atoms). Only the p_x-"partial wave" contribution $\Delta_{p_x}\rho$ to the total density contributes to the force value, since the force operator $\hat{F}_{\rm A}^{\rm el}$ is proportional to $x_{\rm A}/r_{\rm A}^3$, i.e., to Y_{p_x}, where $Y_{p_x}(\theta, \phi)$ is a real spherical harmonic. Therefore $\Delta_{p_x}\rho$ was projected out with the help of an even tempered auxiliary one-center p_x-basis for the density, with overlap matrix $\langle p_x|p_x\rangle$, symbolically (where $p_x = p_x(r)Y_{p_x}(\theta,\phi)$)

$$\Delta_{p_x}\rho(r) = \sum_{p_x} p_x(r)\{\langle p_x|p_x\rangle\}^{-1}\langle p_x|\rho\rangle \qquad (27)$$

Specific spatial contributions to the force integrals were then obtained by splitting the total 3D space up into specific regions (see Figure 3), thereby representing the force or gradient function by a few representative numbers. A numerical integration grid

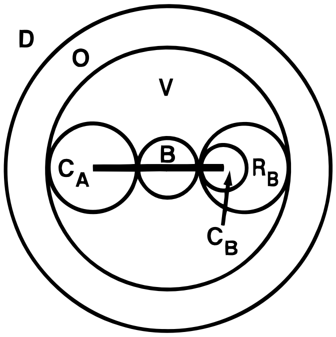


Figure 3. Division of space into chemically relevant parts for a diatomic molecule. C_A, C_B, core (and inner valence) shells of atoms A, B; R_B, back side of atom B; B, central bond region; V, outer valence region; O, outer region; D, distant region. The following radii were chosen for N_2: 32 pm for C_N, 24 pm for B, 88 pm for V, 265 pm for O. For HCl: 42 pm for C_{Cl}, 21 pm for C_H, 42 pm for R_H, 33 pm for B, 117 pm for V, 265 pm for O.

generated by Boerrigter's technique[23] was used so that both the nuclear vicinity as well as the borders of the spatial regions do not cause artifacts.

With *core density* we mean here the total, well-defined electron density in the "core" regions near the atomic nuclei. It consists of the density of the atomic core orbitals and of the inner tails of the molecular valence orbitals. In contrast, the atomic core *orbitals* are not uniquely defined, because—in the Hartree–Fock or Kohn–Sham approaches—they can be transformed unitarily. That is, physical core density polarizations can be described either mainly by core orbitals or mainly by valence orbitals.

Similarly the "inner shells" of the atoms here do not mean respective orbitals but the density in respective spatial regions. The radii of the spatial K, L, and M shells were defined as the (average) r-values of the inner node(s) of the canonical valence orbitals of the neutral atomic ground states, e.g., r(N-K-shell) from N-2s or r(Cl-L-shell) from Cl-3s,3p.

6. H–F Forces in N_2 and HCl

The calculated nuclear equilibrium distances R_e of N_2 and HCl are 1.107 and 1.297 Å (experimental values are 1.098 and 1.275 Å, respectively). In comparison with the energy gradients, the forces were found to be in good (error <0.005 a.u. for N_2) or reasonable (error <0.02 a.u. for HCl) agreement over a large range of internuclear distances.

6.1. Radial Summation of Force Contributions. Figure 4 shows the Hellmann–Feynman force (F_A or F_B, i.e., $\eta = \pm 1$) for N_2 and HCl at equilibrium internuclear distance R_e, radially integrated up to r_A around the respective nucleus as a function of r_A, i.e. using $f(r)$ of eq 19, for instance

$$F_A(r_A) = \int_0^{r_A} dr'_A\, r'^2_A \int d\Omega'\, f(\mathbf{r}') \qquad (28)$$

The nuclear repulsion force of the neighbor nucleus is effectively shielded by the large promolecular contributions of the electronic force, each of which (F^{el} and F^{nuc}) integrates up to ∓ 576 eV/Å (or ∓ 146 eV/Å) in the case of N_2 (or HCl, respectively). For any diatomic molecule the promolecular force (of spherical neutral atoms) shows a rather simple behavior: up to the radius $r_A = R_{AB}$, the total electron density around the neighbor nucleus A shields the nuclear repulsion force,

$$F_B^{pro} = \frac{Z_B}{R_{AB}^2}\left[Z_A - \int_0^{R_{AB}} dr_A\, 4\pi r_A^2\, \rho_A(r_A)\right] \qquad (29)$$

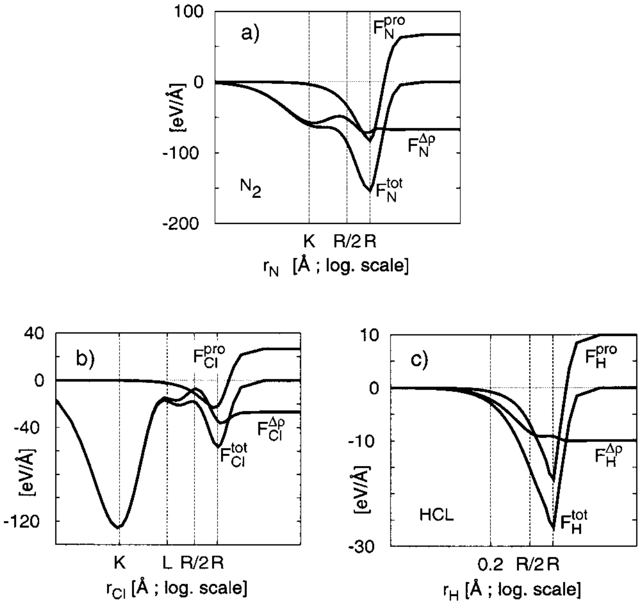


Figure 4. Radially integrated total force (F_A^{tot}) and its promolecular (F_A^{pro}) and deformation density contribution ($F_A^{\Delta\rho}$) for (a) N_2 (top) and (b, c) HCl (bottom) at the computed equilibrium internuclear distances R, see eq 27. The symbols K, L, ... denote the radii of the core shells (defined in section 5). Note the logarithmic scale of the abscissa, r_A being the distance from nucleus A. The gauge parameter η (see section 2) is ± 1.

while electron density outside this radius does not contribute (Faraday cage effect). It means that the antibinding F^{nuc} outweighs the attractive promolecular electronic force F_B^{pro} a little. The total integral ($r_A \to \infty$) of F^{pro} therefore is positive, i.e., antibinding;[16] see Figure 4.

The "missing" binding force to create a stable molecule at $R = R_e$ is due to the deformation density $\Delta\rho$; as mentioned above, $F^{\Delta\rho} = -F^{pro}$. Large contributions to the total integral value of $F^{\Delta\rho}$ are already created in the core region, for the N_2 molecule for instance about 90% in the K-shell of the N atom, due to the dipolar core polarization, and only about 10% in regions $r_N > R/3$, that is in the bond region and in the regions behind the nuclei (see Figure 4). This situation motivated Spackman and Maslen,[17] after a "visual inspection" of the corresponding maps of $\Delta\rho$ (Figure 5), $\hat{F}$ (Figure 2) and $\hat{F}\cdot\Delta\rho$ (Figure 6), to state rather generally that regions far away from the nuclei play "little or no role" in binding.

In the case of HCl (bottom of Figure 4) the huge contributions to the binding force on Cl, $F_{Cl}^{\Delta\rho}$, from the region of the chlorine K shell are almost completely canceled by antibinding forces due to opposite polarizations in the chlorine L shell, while the remaining 14% of the binding forces come from regions with $r_{Cl} > R/2$ around the Cl nucleus. Concerning the force on hydrogen, $F_H^{\Delta\rho}$, it comes from the bond region, as expected. It is well-known (see, e.g., ref 16) that hydrides and especially H_2 are somewhat untypical examples of chemical binding. This is because of the absence of core shells and because of the existence of only a single s-valence shell on the H atom. A bonded hydrogen always shows accumulation of charge density in the bond region, what is clearly not a necessary condition for binding of atoms with open p- or d-shells.[17,26]

The $1/r^2$ factor in the expression of $\hat{\mathbf{F}}^{el}$ strongly weights the neighborhood regions of the nuclei and causes huge positive and negative values of the force integrand on opposite sides of the nuclei at small r-values, which nearly cancel each other upon integration, while any dipolar polarization of the core electron

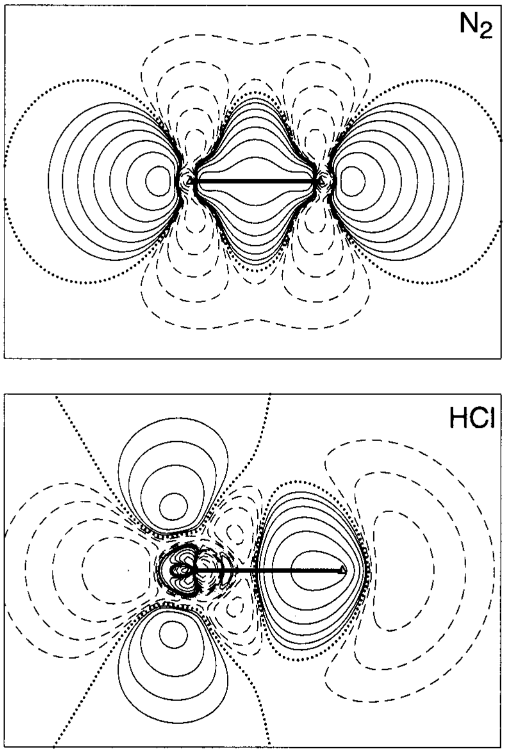


Figure 5. Contour maps of the electron deformation density $\Delta\rho$ of N_2 and HCl at equilibrium internuclear distance. Contour line values are 0.000, $\pm$ 0.002 $\times$ 2^n electrons per bohr^3, $n = 0, 1, 2$ ... (the maximum $\Delta\rho$ of N_2 is about 0.9 e Å^{-3}). The zero contours are dotted; negative contours are dashed.

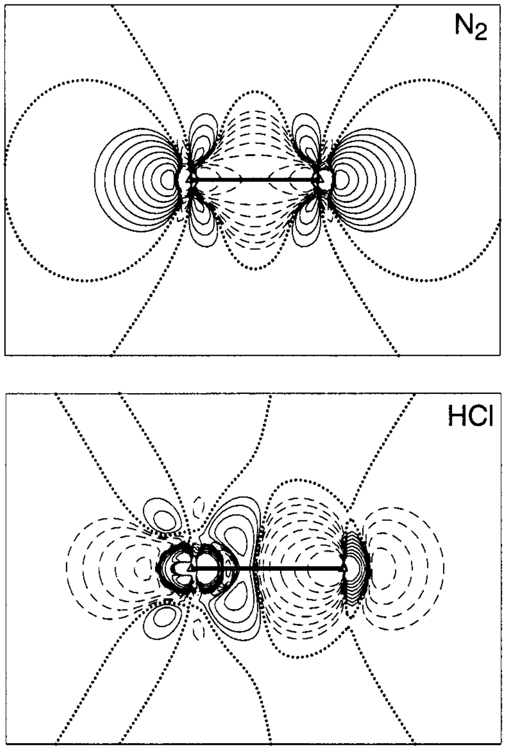


Figure 6. Contour maps of $\hat{F}\Delta\rho$ for N_2 and HCl at equilibrium internuclear distance. η^{CC} gauge for $\hat{F}$ corresponding to Berlin diagram in Figure 2a. Contour line values are 0.00, $\pm$ 0.02 $\times$ 2^n Hartrees per bohr^4, $n = 0, 1, 2, \ldots$ The zero contours are dotted, negative contours are dashed.

density will yield an important contribution to the binding force. However, it is a rash argument that core polarization is the sole reason for chemical binding forces.

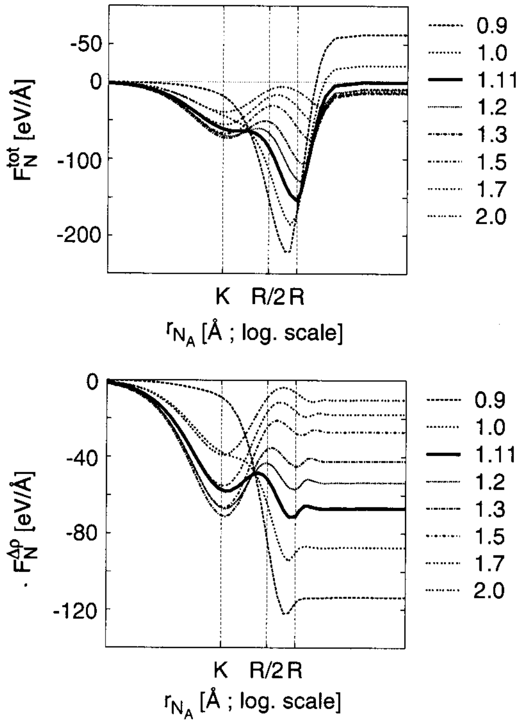


Figure 7. Radially integrated total force (F_N^{tot}) and the contribution from the deformation density ($F_N^{\Delta\rho}$) for N_2 at various internuclear distances. The curve for the equilibrium distance is bold. See also the caption of Figure 4.

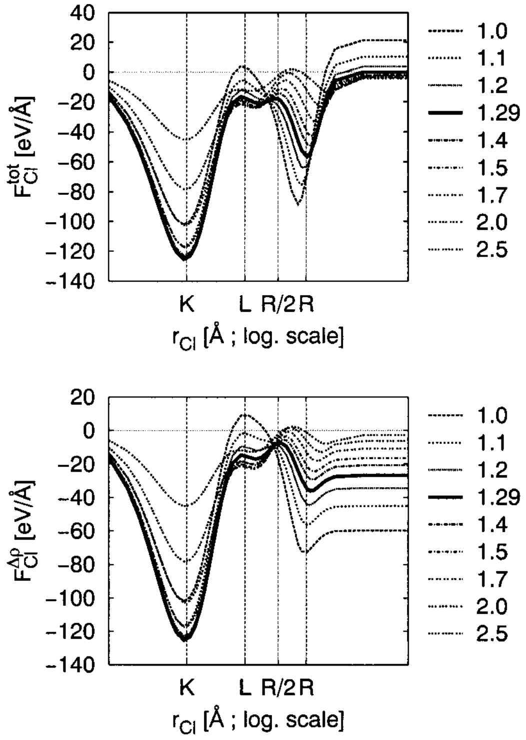


Figure 8. Radially integrated total force (F_{Cl}^{tot}) and the contribution from the deformation density ($F_{Cl}^{\Delta\rho}$) for HCl at various internuclear distances. The curve for the equilibrium distance is bold. See also the caption of Figure 4.

Radially integrated contributions to F^{tot} and $F^{\Delta\rho}$ are shown for different internuclear distances of N_2 and HCl in Figures 7 and 8. The contributions from the nuclear vicinity as well as those from the bond regions and from regions far from the nuclei vary with internuclear distance and are both appreciable.

TABLE 1: Contributions to the Hellmann−Feynman Force Integral from Different Spatial Regions as Represented in Figure 3, for N_2 and HCl at Equilibrium Internuclear Distance[a]

	ρ	$\Delta\rho$	F_A^{el}	$F_A^{\Delta\rho}$	F_{AB}^{el}	$F_{AB}^{\Delta\rho}$	F_B^{el}	$F_B^{\Delta\rho}$
N_2								
$C_{N(A)}$	2.4286	0.0173	−1.2806	−1.0006	−2.5888	−0.5159	−3.8969	−0.0312
$C_{N(A)}$	2.4286	0.0173	−3.8969	−0.0312	−2.5888	−0.5159	−1.2806	−1.0006
B	0.2337	0.0546	−1.5144	−0.3519	−1.5144	−0.3519	−1.5144	−0.3519
V	4.0836	0.0418	−7.8708	−0.4655	−7.8708	−0.4655	−7.8708	−0.4655
O	4.2146	−0.0190	3.2694	0.5374	3.2694	0.5374	3.2694	0.5374
D	0.6109	−0.1120	0.0818	0.0100	0.0818	0.0100	0.0818	0.0100
Σ	14.0000	0.0000	−11.2115	−1.3019	−11.2115	−1.3019	−11.2115	−1.3019
HCl								
$C_{Cl(A)}$	10.0115	−0.0029	−0.4291	−0.3157	−1.5975	−0.0167	−1.6663	0.0009
$C_{H(B)}$	0.0609	0.0122	−0.1757	−0.0368	−0.0689	−0.0456	−0.0626	−0.0462
R_H	0.1443	−0.0012	−0.3259	−0.0108	−0.0713	−0.0217	0.0947	−0.0224
B	0.2429	0.0309	−2.1746	−0.1853	−0.3317	−0.0506	−0.2233	−0.0426
V	3.9762	0.0583	−9.2114	0.1704	−1.2475	−0.0480	−0.7791	−0.0608
O	3.5096	−0.0835	9.4645	−0.1389	0.3436	−0.0288	−0.1929	−0.0223
D	0.0546	−0.0138	0.0215	−0.0041	0.0003	−0.0003	−0.0009	−0.0001
Σ	18.0000	0.0000	−2.8304	−0.5211	−2.8304	−0.2116	−2.8304	−0.1934

[a] The gauge parameter was chosen as $\eta = \pm 1$ (F_A and F_B, respectively) or η^{CC} (F_{AB}).

6.2. Force Contributions from Different Regions of Space. In Table 1 the electronic forces F^{el} and $F^{\Delta\rho}$ at $R = R_e$ are split up into contributions from different regions of the molecule, cf. Figure 3. In both diatomics, N_2 and HCl, we have applied three different gauge parameters: $\eta = \pm 1$ and η^{cc} (eq 6b), the latter corresponding to the symmetric Berlin diagram of Figure 2a. In the case of N_2 the core polarization is indeed the largest contribution to $F^{\Delta\rho}$, but the density changes in the inner bond region (B), in the outer valence region (V), and on the back sides of the atoms (contained in the O region) give rise to contributions to the total F^{el} of the same order of magnitude than those from the atomic cores. At R_e, the antibinding forces from the atomic back sides, which are due to a lone pair charge accumulation in this electrostatically antibinding region, cancel a large part of the binding forces in the bond and valence region, so that the sum of these forces approximately vanishes in the radial contributions to $F^{\Delta\rho}$, cf. Figure 4.

A similar situation holds for HCl. Especially for the choice of η^{CC} (F_{AB}) the bond and the outer valence regions dominate the binding forces from $\Delta\rho$, while the core polarization gives an important but, in contrast to N_2 not the dominant contribution to $F_{Cl}^{\Delta\rho}$ (η^{cc} weights F_{Cl} much less ($\times {}^{1}/_{18}$) than F_H ($\times {}^{17}/_{18}$), and H without core orbitals is an atypical bond mate). Again, other regions far away from the nuclei contribute binding and antibinding forces of the same order of magnitude, which, in their sum, determine the sensitive balance of forces at equilibrium geometry. Figures 7 and 8 indicate that at other internuclear distances the changing topology of $\Delta\rho$ weights other regions of space differently, sometimes in a way that major binding effects take place at distances $\gtrsim R/2$ from the nuclei.

6.3. Core Polarization. Figure 9 shows significant dipolar polarization of the core densitiy of N in N_2 and of Cl in HCl. In Figure 10 the radially integrated electronic contribution of the force, eq 28, as obtained from the partial wave decomposition of the density, eq 27, is compared with the respective result from numerical integration of the total density as in Figure 4. In N_2 the polarized 1s core shell contributes approximately 11% (i.e., −1.28 au) to the total electronic force of −11.2 au. This represents a major contribution to $F^{\Delta\rho}$, namely 76% (i.e., −1.00 au, see Table 1). The individually much larger binding and antibinding forces around the Cl nucleus in HCl (Figures 4b and 10b) result from the orthogonality of the chlorine K and L shells, which causes polarizations of opposite signs in different shells (see also ref 27).

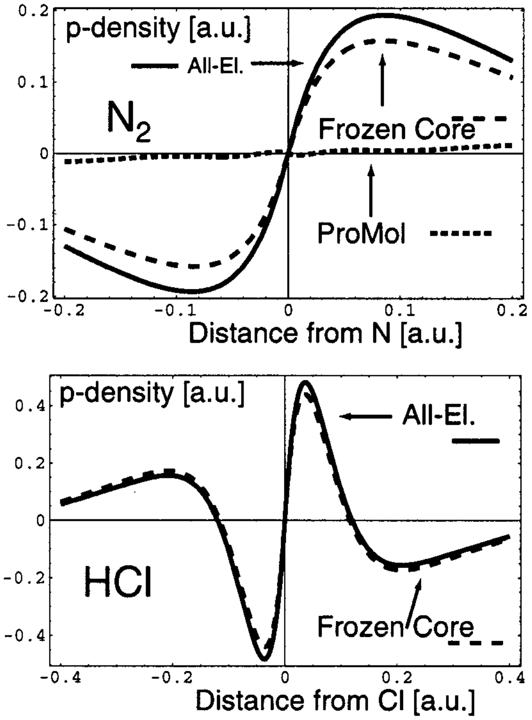


Figure 9. Dipolar polarization of (a) the N and (b) the Cl core density (p-wave contribution) in N_2 and HCl at equilibrium internuclear distance, from "all-electron" and from "frozen atomic core orbital" calculations. ProMol means the "promolecular" superposition of spherical unperturbed atomic densities, the tail of the other atom's density causing only a small density polarization.

The all-electron calculations and the (appropriately designed) frozen atomic core—valence only optimized—calculations (N, 1s; Cl, 1s2s2p frozen) are known to yield quite similar binding energies and equilibrium structures. Figure 9 demonstrates that the core polarizations are also similar in both approaches. In the case of valence only calculations, the specific molecular features in the atomic valence shells causes a specifically polarized valence density distribution. The orthogonalization of the asymmetric molecular valence orbitals on the spherical atomic core orbitals creates polarized tails of the valence orbitals in the core regions. In other words, the sign topology of the molecular valence shell is coupled to the corresponding sign pattern of density polarizations in the atomic core shells as a

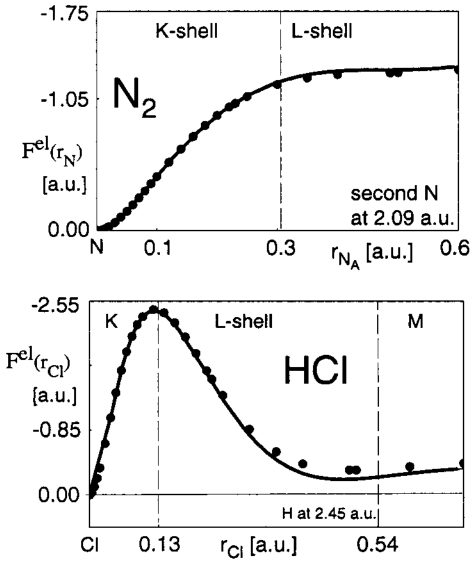


Figure 10. Radially integrated Hellmann−Feynman force density in the core regions of (a) N in N_2 and of (b) Cl in HCl. The points were calculated by numerical integration of the density, and the curves were obtained by analytical integration of the p-wave contribution to the core density polarization shown in Figure 9.

consequence of the orthogonality restriction arising from the Pauli principle (compare also Hellmann[28] in 1936).

In an all-electron calculation the molecular core density polarization is represented by the sum of core orbital polarizations and polarized tails of the valence orbitals. In a recent reinvestigation of contributions of the canonical SCF orbitals to F^{el} [13] it was found that a significant part of F^{el} resulted from the density of the inner core molecular orbitals, e.g., in N_2 from $1\sigma_g$ and $1\sigma_u$, what was called the "atomic dipole" (AD) contribution. These results are in agreement with Figures 9 and 10, where a fraction of the core polarization is due to polarization of the core orbitals.

Figure 9 shows that the core orbital polarization of N_2 is not completely accounted for in the valence only calculation. This is the error of the frozen core approximation, which seems to be compensated by a respective change (i.e., error) of the valence charge density so that the molecular energy and force curves are still quite accurate.

7. Concluding Remarks

The chemical bond energy gradients or binding forces between the atomic nuclei, which have well-defined values and vanish at equilibrium structure, can be obtained by 3D integration over a strongly gauge-dependent function, eq **D**:19. It may be called the energy gradient/force density. It contains terms proportional to $\rho(\mathbf{r})$, to $\partial\rho(\mathbf{r})/\partial R$, and/or to $\rho(\mathbf{r})/r^2$.

The first two terms represent the energy gradient density. Significant contributions to the kinetic and potential bonding energy gradients come from the valence regions of the molecule. Bonding can be explained through density changes in the bond overlap and lone pair regions.

Since the valence molecular orbitals should be chosen orthogonal to the inner core orbitals in order to obtain a simple picture in the orbital model, the pattern of core density polarizations is coupled to the pattern of the valence density deformations. Bonding/binding can (partially) be explained through valence shell effects or (partially) through core density effects, namely, when the neighborhood of the nuclei is weighted by a $1/r^2$-factor in the Hellmann−Feynman binding force expression.

In the gradient expression, the kinetic energy gradient partially cancels the potential energy gradients, and a numerically sensitive potential term is left over in the Hellmann−Feynman force expression. The coupling of density deformations in the valence and core regions in the holistic theory of quantum mechanics allows one to explain bonding/binding, for instance, along either of the following two lines. One may analyze the interplay of several different energy or energy gradient contributions from the inner and outer valence regions, the determination of which is numerically stable. Or one may discuss simple electrostatic force contributions from all molecular regions (the inner and outer core shells, together with contributions from the valence regions), which are not easy to compute accurately (however, see, e.g., ref 29).

The core density polarization can be represented either dominantly by core orbitals or dominantly by the orthogonality tails of the valence functions. A frozen core orbital approximation still reproduces a large part of the core density polarization. Bonded hydrogen atoms constitute a somewhat unusual case of bonding, since there are no core shells. Finally we note that the first derivation and discussion of the electrostatic force theorem was published by Hellmann in a rather common journal already in 1933.[2]

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