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Orbital forces and chemical bonding in density-functional theory: Application to first-row dimers

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The local-density-functional description of chemical bonding in first-row homonuclear dimers is analyzed in terms of both static and dynamic orbital forces. The dynamic orbital force of the ith molecular orbital is equal to the negative of the derivative of the one-electron energy ε_i with respect to the pth nuclear coordinate, i.e., $-\partial\varepsilon_i/\partial X_p$. The static orbital force is also equal to a derivative of the one-electron energy, but the differentiation is carried out with the orbital held fixed, i.e., $(-\partial\varepsilon_i/\partial X_p)_\psi$. It is shown that the static force is the orbital's contribution to the total Hellmann-Feynman force, whereas the dynamic force describes the change in the total force due to change in the orbital's occupation number. The chemical bond force in the first-row dimers is observed to be a delicate balance between bonding and antibonding orbital forces. Most of the bond force comes from the $2\sigma_g$ orbital and to a lesser extent from the $1\pi_u$ state. The polarization of the core orbitals in N_2, O_2, and F_2 is found to originate indirectly through their interaction with the $3\sigma_g$ orbital. The dynamic orbital force gives accurate predictions about the change of equilibrium bond distances accompanying electronic ionization and excitation. The formalism and results are related to earlier Hartree-Fock studies.

I. INTRODUCTION

The Hellmann-Feynman (HF) theorem[1,2] states that the exact force on a nucleus in a system of electrons and nuclei is simply the classical electrostatic interaction of the nuclear charge with the field set up by the other nuclei and the electronic charge density, $\rho(\mathbf{r})$, which is itself determined quantum mechanically. The x component of this force (on the pth nucleus) is expressed in atomic units as

$$F_x^p(\mathrm{HF})=\int \rho(\mathbf{r})\frac{\partial}{\partial X_p}\left[\frac{Z_p}{|\mathbf{r}-\mathbf{R}_p|}\right]d\mathbf{r} - \sum_{q(\neq p)}\frac{\partial}{\partial X_p}\left[\frac{Z_pZ_q}{|\mathbf{R}_p-\mathbf{R}_q|}\right] . \quad (1)$$

In the density-functional formalism,[3] the ground-state charge density $\rho(\mathbf{r})$ is expressed in terms of the solutions of the one-electron Kohn-Sham equations and occupation numbers n_i as

$$\rho(\mathbf{r})=\sum_i n_i\,|\psi_i(\mathbf{r})|^2 . \quad (2)$$

The explicit decomposition of the charge density in terms of one-electron orbital charge densities allows the electronic part of the Hellmann-Feynman force to be similarly decomposed into orbital forces,[4,5]

$$F_{x,i}^p(\mathrm{HF})=\int |\psi_i(\mathbf{r})|^2\frac{\partial}{\partial X_p}\left[\frac{Z_p}{|\mathbf{r}-\mathbf{R}_p|}\right]d\mathbf{r} . \quad (3)$$

The total Hellmann-Feynman force then becomes

$$F_x^p(\mathrm{HF})=\sum_i n_iF_{x,i}^p(\mathrm{HF})+F_x^p(\mathrm{NN}) , \quad (4)$$

where $F_x^p(\mathrm{NN})$ is the nuclear-nuclear repulsive term in Eq. (1).

The significance of this last equation is that it allows a chemical bond to be resolved into one-electron orbital contributions. Bader and co-workers[4,6,7] have shown that an analysis of comparable orbital forces in Hartree-Fock theory can be useful in elucidating characteristics of chemical bond formation. In particular, they showed that these orbital forces, when compared to a prescribed reference force, could be taken to define a quantitative measure of the bonding or antibonding character of a molecular orbital.

Later, Tal and Katriel[8] introduced another orbital force defined in terms of the one-electron energy ε_i as $(-\partial\varepsilon_i/\partial X_p)$. They demonstrated that this orbital force, which is related to the change in bond force upon ionization, is more consistent with the traditional concepts of bonding and antibonding suggested by Mulliken.[9]

The purpose of the present paper is to first develop the concepts of orbital force in the density-functional theory (DFT) and secondly to apply these concepts to a study of the first-row homonuclear diatomic molecules. The orbital forces computed in the local-spin-density approximation (LSDA) will be compared and contrasted with those obtained in the Hartree-Fock approximation.

II. THEORY OF ORBITAL FORCES IN THE DENSITY-FUNCTIONAL FORMALISM

In the density-functional formalism, the one-electron equation,

$$H(\mathbf{r})\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r}) , \quad (5)$$

is obtained by requiring that the total energy E be a minimum (corresponding to the ground-state density and energy E) with respect to variations in the ith orbital. The one-electron Hamiltonian can be written (in atomic units)

$$H(\mathbf{r})=-\tfrac{1}{2}\nabla^2-\sum_q \frac{Z_q}{|\mathbf{r}-\mathbf{R}_q|}+V_{ee}(\mathbf{r})+V_{\mathrm{xc}}(\mathbf{r}) \ , \qquad (6)$$

where $V_{ee}(\mathbf{r})$ is the classical Coulomb potential of the charge density $\rho(\mathbf{r})$, and $V_{\mathrm{xc}}(\mathbf{r})$ is the exchange-correlation potential, which depends upon the charge density.

Multiplying both sides of Eq. (5) by $\psi_i^*(\mathbf{r})$ and integrating over all space gives the one-electron energy eigenvalue as

$$\varepsilon_i=\int \psi_i^*(\mathbf{r})H(\mathbf{r})\psi_i(\mathbf{r})d\mathbf{r} \ . \qquad (7)$$

From this, it is easy to show that

$$\left[-\frac{\partial \varepsilon_i}{\partial X_p}\right]_\psi = F^p_{x,i}(\mathrm{HF}) \ , \qquad (8)$$

with the subscript ψ indicating that the partial derivative is taken while holding the orbitals ψ_i fixed in space. By reason of this constraint, the force defined by Eq. (8) is called the *static* orbital force. This eigenvalue derivative with constrained orbitals is in the spirit of the familiar result[10] relating the one-electron eigenvalues to the dependence of the total energy on occupation numbers,

$$\left[\frac{\partial E}{\partial n_i}\right]_\psi = \varepsilon_i \ . \qquad (9)$$

In what follows, it will be important to know the details of the derivation of Eq. (9). Janak[11] has shown that the unconstrained derivative of the total energy E is given by

$$\frac{\partial E}{\partial n_i}=\varepsilon_i+\sum_j n_j \, \varepsilon_{ij}(\mathrm{BS}) \ , \qquad (10)$$

where (BS denotes basis set)

$$\varepsilon_{ij}(\mathrm{BS})=\int \frac{\partial \psi_j^*(\mathbf{r})}{\partial n_i}H(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r} \ . \qquad (11)$$

Clearly, if the orbitals are held fixed during the differentiation, the derivative in Eq. (11) will be zero and Eq. (10) will reduce to Eq. (9). If the orbitals are not held fixed, ε_{ij}(BS) will still be zero if the basis is complete and the orbitals are rigorously eigenfunctions of the Hamiltonian $H(r)$. Then Eq. (11) becomes

$$\varepsilon_{ij}(\mathrm{BS})=\varepsilon_j\int \frac{\partial \psi_j^*(\mathbf{r})}{\partial n_i}\psi_j(\mathbf{r})d\mathbf{r}+\mathrm{c.c.} \qquad (12)$$

The right-hand side of Eq. (12) can be written as the derivative of the normalization integral of $\psi_j(\mathbf{r})$ and must, therefore, be zero.

It is important to note that the step from Eq. (11) to Eq. (12) is possible only if $\psi_j(\mathbf{r})$ is an exact eigenfunction of $H(r)$. If $\psi_j(\mathbf{r})$ is expanded in terms of an incomplete basis set, ε_{ij}(BS) will not, in general, be zero and Eq. (12) will not be satisfied. However, assuming a complete basis-set expansion for $\psi_i(\mathbf{r})$, the constrained and unconstrained derivatives of the total energy will be equal giving

$$\frac{\partial E}{\partial n_i}=\left[\frac{\partial E}{\partial n_i}\right]_\psi=\varepsilon_i \ . \qquad (13)$$

The incompleteness of practical basis sets generally causes the Hellmann-Feynman force to diverge somewhat from the true total-energy derivative $\partial E/\partial X_p$. However, this problem can be overcome by the formal computation of the total-energy derivative (or gradient force),[5,12,13]

$$-\frac{\partial E}{\partial X_p}=F^p_x(\mathrm{HF})-\sum_j n_j\left[\int \frac{\partial \psi_j^*(\mathbf{r})}{\partial X_p}H(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}+\mathrm{c.c.}\right] . \qquad (14)$$

The terms in large parentheses correct the Hellmann-Feynman force by including the explicit dependence of the orbitals upon the nuclear coordinate X_p. If $\psi_j(\mathbf{r})$ were a true eigenfunction of $H(\mathbf{r})$, then the term in large parentheses would be zero, and Eq. (14) would reduce to the Hellmann-Feynman theorem. However, for most practical basis sets, this term will be nonzero and must be included for accurate force values.

Like the Hellmann-Feynman force, the basis-set correction can be decomposed into orbital components, e.g., for state "j",

$$F^p_{x,j}(\mathrm{BS})=-\left[\int \frac{\partial \psi_j^*(\mathbf{r})}{\partial X_p}H(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}+\mathrm{c.c.}\right] . \qquad (15)$$

The total force can then be expressed as the sum over occupied states (with occupation numbers n_j),

$$-\frac{\partial E}{\partial X_p}=\sum_j n_j F^p_{x,j}+F^p_x(\mathrm{NN}) \ , \qquad (16)$$

where

$$F^p_{x,j}=\left[-\frac{\partial \varepsilon_i}{\partial X_p}\right]_\psi+F^p_{x,j}(\mathrm{BS}) \ . \qquad (17)$$

This equation defines the basis-set corrected form of the static orbital force. If the unconstrained derivatives in Eqs. (14) and (16) are replaced by constrained derivatives, Eq. (16) becomes

$$\left[-\frac{\partial E}{\partial X_p}\right]_\psi=\sum_j n_j\left[-\frac{\partial \varepsilon_j}{\partial X_p}\right]_\psi+F^p_x(\mathrm{NN}) \ . \qquad (18)$$

Comparison of Eqs. (16) and (18) suggests a possible equality between $-\partial\varepsilon_j/\partial X_p$ and $F^p_{x,j}$. Actually, this turns out *not* to be the case as will be shown in the following.

Taking the derivative of both sides of Eq. (7) leads to the definition of the *dynamic* orbital force,[14]

$$-\frac{\partial \varepsilon_j}{\partial X_p}=-\int \psi_j^*(\mathbf{r})\frac{\partial H}{\partial X_p}\psi_j(\mathbf{r})d\mathbf{r}+F^p_{x,j}(\mathrm{BS}) \ . \qquad (19)$$

Again as in Eq. (17), the term $F^p_{x,j}$(BS) is seen to correct an orbital force for basis-set incompleteness. However, the *dynamic* orbital force defined by Eq. (19) is demonstrably very different from the *static* orbital force $(-\partial\varepsilon_j/\partial X_p)_\psi$. The difference can be made more explicit by rewriting Eq. (19). Factoring the electron-nuclear potential from $H(\mathbf{r})$, Eq. (19) becomes

$$-\frac{\partial \varepsilon_j}{\partial X_p}=F^p_{x,j}(\mathrm{HF})+F^p_{x,j}(\mathrm{BS})+F^p_{x,j}(\mathrm{EE}) \ , \qquad (20)$$

where

$$F^p_{x,j}(\mathrm{EE}) = -\int \psi_j^*(\mathbf{r}) \left[\frac{\partial V_{ee}(\mathbf{r})}{\partial X_p} + \frac{\partial V_{xc}(\mathbf{r})}{\partial X_p} \right] \psi_j(\mathbf{r}) d\mathbf{r} \,. \tag{21}$$

Then using Eq. (8), we have

$$-\frac{\partial \varepsilon_j}{\partial X_p} = \left[-\frac{\partial \varepsilon_i}{\partial X_p} \right]_\psi + F^p_{x,j}(\mathrm{BS}) + F^p_{x,j}(\mathrm{EE}) \,. \tag{22}$$

The static and dynamic orbital forces differ by the sum of the basis-set correction term $F^p_{x,j}(\mathrm{BS})$ and a force term, $F^p_{x,j}(\mathrm{EE})$, which depends on the derivatives of the effective interelectron potentials. For a complete basis set, $F^p_{x,j}(\mathrm{BS})$ will be zero, but the static and dynamic forces will still differ by the term $F^p_{x,j}(\mathrm{EE})$. Recalling that Eq. (1) can also be written

$$F^p_x(\mathrm{HF}) = \left[-\frac{\partial E}{\partial X_p} \right]_\psi , \tag{23}$$

the *static* orbital force appearing in Eq. (18) emerges as the jth orbital's contribution to the Hellmann-Feynman force.

In the following, we address the question of how the *dynamic* force is related to the Hellmann-Feynman and total forces. Taking the derivative of both sides of Eq. (10) with respect to X_p gives

$$\frac{\partial^2 E}{\partial X_p \partial n_i} = \frac{\partial \varepsilon_i}{\partial X_p} + \sum_j n_j \frac{\partial}{\partial X_p} \varepsilon_{ij}(\mathrm{BS}) \,. \tag{24}$$

Assuming that the order of differentiation in $\partial^2 E / \partial X_p \partial n_i$ can be reversed,[15] Eq. (24) can be written as

$$\frac{\partial F^p_x}{\partial n_i} = -\frac{\partial \varepsilon_i}{\partial X_p} - \sum_j n_j \frac{\partial}{\partial X_p} \varepsilon_{ij}(\mathrm{BS}) \,. \tag{25}$$

For a complete basis set, $\varepsilon_{ij}(\mathrm{BS})$ and all its *unconstrained* derivatives[16] will be zero. Then Eq. (25) becomes

$$\frac{\partial F^p_x}{\partial n_i} = -\frac{\partial \varepsilon_i}{\partial X_p} \,. \tag{26}$$

The dynamic orbital force therefore describes how the total force changes in response to a change in the occupation number n_i. The change in the force F^p_x upon ionization of an electron from the ith state (at fixed bond distance) is[8]

$$F^{p+}_{x,i} - F^p_x = \int_1^0 -\frac{\partial \varepsilon_i}{\partial X_p} dn_i \,. \tag{27}$$

This result is the analogue to the expression for differences in total energy given by[11]

$$E_i^+ - E = \int_1^0 \varepsilon_i \, dn_i \,. \tag{28}$$

Let us look further into the relation between the static and dynamic orbital forces. From Eq. (9), it follows that

$$\left[-\frac{\partial \varepsilon_i}{\partial X_p} \right]_\psi = \left[-\frac{\partial}{\partial X_p} \left[\frac{\partial E}{\partial n_i} \right]_\psi \right]_\psi = \left[-\frac{\partial^2 E}{\partial n_i \partial X_p} \right]_\psi \,. \tag{29}$$

Using Eq. (23), this can be rewritten as

$$\left[-\frac{\partial \varepsilon_i}{\partial X_p} \right]_\psi = \left[\frac{\partial F^p_x(\mathrm{HF})}{\partial n_i} \right]_\psi \,. \tag{30}$$

Comparing Eqs. (26) and (30), it might at first sight appear that the static and dynamic forces should be equal, since for a complete basis set $F^p_x = F^p_x(\mathrm{HF})$ (i.e., the gradient and Hellmann-Feynman forces are equal). This would be contrary to Eq. (22), however, which shows that the static and dynamic forces are, in general, *not* equal. The apparent paradox is resolved by remembering the conditions for equality of gradient and Hellmann-Feynman forces, $F^p_x = F^p_x(\mathrm{HF})$. The Hellmann-Feynman theorem is satisfied only if all $\psi_j(\mathbf{r})$ are eigenfunctions of $H(\mathbf{r})$. This condition will be satisfied in the unconstrained differentiation $\partial F^p_{x,j}(\mathrm{BS})/\partial n_i$ but not in the constrained derivative $[\partial F^p_{x,j}(\mathrm{BS})/\partial n_i]_\psi$, where the orbital does not adjust to the changing occupation number. Consequently, even for a complete basis set

$$\left[\frac{\partial F^p_x(\mathrm{HF})}{\partial n_i} \right]_\psi \neq \frac{\partial F^p_x(\mathrm{HF})}{\partial n_i} \,. \tag{31}$$

However, for the unconstrained derivative in a complete basis set

$$\frac{\partial F^p_x(\mathrm{HF})}{\partial n_i} = \frac{\partial F^p_x}{\partial n_i} , \tag{32}$$

and for the gradient force

$$\left[\frac{\partial F^p_x}{\partial n_i} \right]_\psi = \frac{\partial F^p_x}{\partial n_i} = -\frac{\partial \varepsilon_i}{\partial X_p} , \tag{33}$$

but

$$\left[\frac{\partial F^p_x}{\partial n_i} \right]_\psi \neq \left[\frac{\partial F^p_x(\mathrm{HF})}{\partial n_i} \right]_\psi = \left[-\frac{\partial \varepsilon_i}{\partial X_p} \right]_\psi \,. \tag{34}$$

III. APPLICATION TO THE FIRST-ROW HOMONUCLEAR DIMERS

A. Computational details

The calculations reported here were carried out using the augmented Gaussian orbital linear variational method[17] within the local-spin-density approximation. The exchange-correlation functional of Vosko, Wilk, and Nusair[18,19] (VWN) was employed in this study. Molecular-orbital basis sets were derived from the atomic basis sets given by van Duijneveldt,[20] with the addition of a single d orbital (and three p functions in the cases of Li and Be). In each case beyond Be, a ($10s,6p,1d/5s,4p,1d$) contraction was carried out by supplementing the optimized (within the LSDA) atomic orbitals with the one free d and the three most diffuse s and p Gaussians. The present basis is essentially the same as that used by the authors in earlier work[21] on the first-row dimers in which an analytic linear combination of atomic orbitals (LCAO)—Gaussian-type orbital approach was used. In principle the augmentation step does not introduce any error in the calculation, and the good agreement of the results reported here with the earlier work further indicates negligible numerical errors occur with the present calculational method in practice.

In Table I, the equilibrium bond distances computed in our earlier work[21] by total-energy minimization are compared with those calculated here using the gradient force method to search for zero total force. The differences in the ground-state bond distances are all 1% or less. Good agreement with the other computed spectroscopic data reported in Ref. 21 is also found, but those results will not be repeated here.

The VWN functional in the LSDA gives the correct ground-state symmetries for $Li_2(^1\Sigma_g^+)$, $Be_2(^1\Sigma_g^+)$, $N_2(^1\Sigma_g^+)$, $O_2(^3\Sigma_g^-)$, and $F_2(^1\Sigma_g^+)$, but not for B_2 or C_2. For B_2 the energy is slightly lower (less than 0.1 eV) for a $^5\Sigma_u^-$ state than for the experimental $^3\Sigma_g^-$ ground state, even though both states have all molecular levels filled below the Fermi energy. In C_2, the experimental ground state $^1\Sigma_g^+$ is higher in energy than a $^3\Pi_u$ state which has a completely filled set of levels below the Fermi energy. This overstabilization of states of higher spin and/or higher angular momentum atomic components is characteristic of the LSDA. However, for both B_2 and C_2, the bond distances calculated for the experimental ground-state configurations are in good agreement with experiment. Unless stated otherwise, all the results reported here have been obtained using the experimental ground-state configurations. For orbitals for which the spin splitting is nonzero (the cases of B_2 and O_2), the forces and energies reported in the tables below are averages over the two spin-state values, if both states are occupied.

For linear variational calculations utilizing a fixed basis set, the basis-set correction term, $F_{x,i}^p(\mathrm{BS})$, can be put into a more computationally convenient form than Eq. (15). The orbital solutions are expanded as linear combinations of basis functions $\chi_j(\mathbf{r})$:

$$\psi_i(\mathbf{r})=\sum_j C_j^i \chi_j(\mathbf{r}) \ . \tag{35}$$

Equation (15) can then be written as[5,12,13]

$$F_{x,i}^p(\mathrm{BS})=-\sum_{j,k} C_j^{i*} C_k^i \int \frac{\partial \chi_j^*(\mathbf{r})}{\partial X_p}[H(\mathbf{r})-\varepsilon_i]\chi_k(\mathbf{r})d\mathbf{r} \\ +\mathrm{c.c.} \tag{36}$$

Evaluation of the matrix elements represented by Eq. (36) forms part of the extra computational step necessary in implementing the calculation of the gradient force.

TABLE I. Comparison of bond distances (in bohr) computed directly from the total force on the nucleus (b_F) with bond distances computed by Painter and Averill (Ref. 21) by energy minimization (b_E) and with experiment (Ref. 22) (b_{expt}).

	b_E	b_F	b_{expt}
Li_2	5.12	5.13	5.05
Be_2	4.63	4.58	4.65[a]
B_2	3.03	3.03	3.04
C_2	2.36	2.36	2.35
N_2	2.08	2.07	2.07
O_2	2.31	2.29	2.28
F_2	2.62	2.63	2.68

[a] Reference 23.

B. Study of N_2: Comparison of various orbital force components

In the remaining discussion, N_2 is selected as a specific case for analysis. Table II gives the orbital forces for N_2 at the equilibrium bond distance. Note that $F_{x,i}^p(\mathrm{EE})$ tends to be of about the same magnitude as the static force but opposite in sign. As a result, the static and dynamic forces are, in general, of very different magnitude [see Eq. (22)]. With the exception of the $3\sigma_g$ orbital, the basis-set correction terms, $F_{x,i}^p(\mathrm{BS})$, are small compared to their associated static forces. This is fortunate, because as long as $F_{x,i}^p(\mathrm{BS})$ remains small compared to $(-\partial\varepsilon_i/\partial X_p)_\psi$, the orbital forces, $F_{x,i}^p$, can be readily analyzed in terms of classical charge and force arguments.[24]

The good agreement between the dynamic force and $\partial F_x^p/\partial n_i$, which are equivalent only if the basis-set correction vanishes, suggests that the basis-set correction term in Eq. (25) is small. The dynamic force can then be used as a good approximation to $\partial F_x^p/\partial n_i$ to make predictions about how the internuclear separations in a molecule will be changed by ionization.

The binding energy of N_2 as a function of the bond distance is given in Fig. 1 and corresponding total forces in Fig. 2. If the molecular orbitals are restricted to $D_{\infty h}$ symmetry, the separated atom limit of the $^1\Sigma_g^+$ ground

TABLE II. Orbital forces for N_2 at equilibrium (units are eV/bohr).

	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$
$(-\partial\varepsilon_i/\partial X_p)_\psi$	−24.60	−24.34	−57.71	7.30	−25.30	−2.35
$F_{x,i}^p(\mathrm{BS})$	−0.12	−0.13	0.60	−0.63	−0.58	−1.09
$F_{x,i}^p$	−24.72	−24.47	−57.11	6.67	−25.88	−3.44
$F_{x,i}^p(\mathrm{EE})$	28.58	28.54	49.46	−2.92	21.74	3.06
$-\partial\varepsilon_i/\partial X_p$	3.86	4.07	−7.65	3.75	−4.14	−0.38
$\partial F_x^p/\partial n_i$	3.85	4.06	−7.59	3.75	−4.13	−0.38

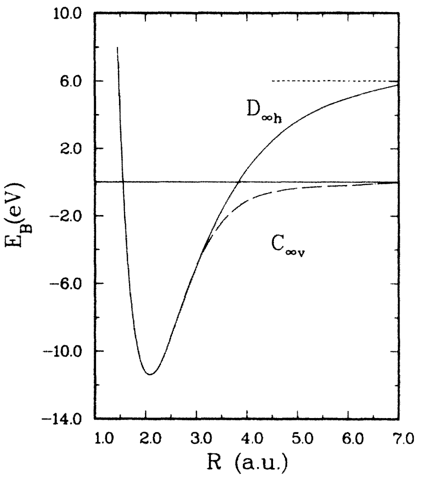

FIG. 1. Binding energies of paramagnetic (solid line) and antiferromagnetic (dashed-dotted line) N_2 as functions of the bond distance (R).

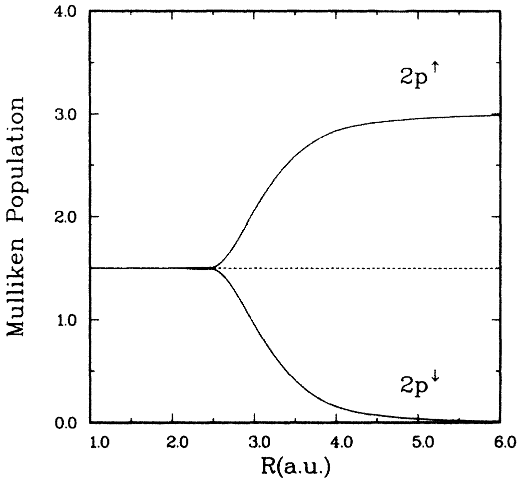

FIG. 3. Mulliken population analysis of the $2p$-spin-up ($2p\uparrow$) and $2p$-spin-down ($2p\downarrow$) atomic orbitals in N_2 as a function of the bond distance (R).

state is that of two zero-spin atoms with occupation numbers in the p shell averaged over spin up and down, i.e., $1s^22s^22p_\uparrow^{1.5}2p_\downarrow^{1.5}$. In order to obtain the correct atomic ground-state population, $1s^22s^22p_\uparrow^3$, the spin reflection symmetry between the two sites must be broken, and the molecular orbitals allowed to have $C_{\infty v}$ symmetry. When this is done, the molecule becomes antiferromagnetic at bond distances greater than about 2.50 bohr. This is illustrated in Fig. 3 by the Mulliken population analysis results for one of the nitrogen atoms, where the $2p$ occupation, $2p_\uparrow^{1.5}2p_\downarrow^{1.5}$, changes to $2p_\uparrow^{3.0}$ at large bond distances.

The Hellmann-Feynman [Eq. (4)] and gradient [Eq. (14)] forces for the ${}^1\Sigma_g^+$ ground state of N_2 are both given in Fig. 2. The basis-set corrected force is lower than the Hellmann-Feynman force by an amount that increases as the bond distance decreases. At the equilibrium bond distance, the basis-set correction is already over 2 eV/bohr. The force curves for the antiferromagnetic state of N_2 (dotted lines) follow the paramagnetic curves at small bond distances, but beyond $b=2.50$, they tend to zero more quickly as the bond distance is increased.

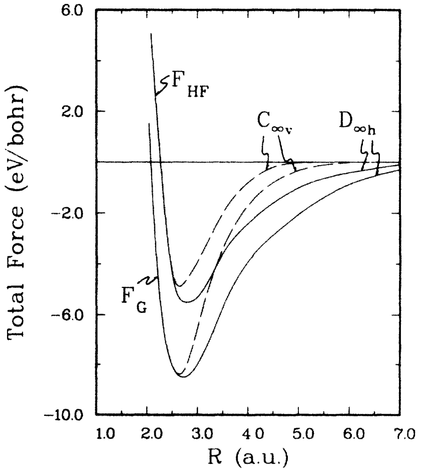

FIG. 2. Hellmann-Feynman (F_{HF}) and gradient (F_G) forces on a nucleus of N_2 as functions of the bond distance (R). These two forces differ by the basis-set correction term given in Eq. (14). The solid curves are for the paramagnetic case, whereas the dashed curves are for the antiferromagnetic dimer.

In Fig. 4, the basis-set corrected static orbital forces ($F_{x,i}^p$) of paramagnetic ($D_{\infty h}$) N_2 are plotted. The forces of the core orbitals $1\sigma_g$ and $1\sigma_u$ have a $1/r^2$-type behavior which can be easily understood: the charge density of one of these orbitals at large separation approaches the superposition of two spherical symmetric charge densities, each of one half an electron charge, centered on the two nitrogen nuclei. In this limit, the force of this orbital charge density on the nucleus approaches, for internuclear separation b, $-\frac{1}{2}Z/b^2$. For nitrogen ($Z=7$), this yields

$$F_x^p(\mathrm{RF}) = -\tfrac{1}{2}Z/b^2 = -\frac{95.24}{b^2}\,\frac{\mathrm{eV}}{\mathrm{bohr}} . \tag{37}$$

This limit can be taken to defined a reference force (F_R in Fig. 4) which approximates well the behavior of the core orbitals in Fig. 4 and is the asymptotic limit of all the static orbital forces in paramagnetic N_2.

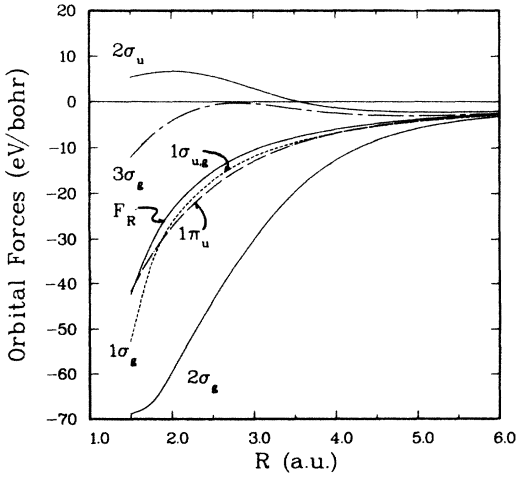

FIG. 4. Static molecular-orbital forces, $F_{x,i}^p$ [see Eq. (16)], in N_2 each as a function of the bond distance (R).

These results suggest that a measure of bond character can be obtained from the static orbital force by subtracting out its asymptotic behavior, $F^p_x(\mathrm{RF})$,

$$F^p_{x,i}(C) \equiv F^p_{x,i} - F^p_x(\mathrm{RF}) \; . \tag{38}$$

This new force is a direct measure of how effectively the orbital binds the nuclei together in the molecule. For this reason, we have chosen to call it an orbital cohesive force.[5] The sign of the orbital cohesive force indicates the bond character (bonding or antibonding) of the relevant state. Another useful property of the orbital cohesive force is that the sum of all orbital cohesive forces in the dimer gives (with $2Z$ electrons in the system) the total gradient force,

$$-\frac{\partial E}{\partial X_p} = \sum_i n_i F^p_{x,i}(C) \; . \tag{39}$$

Each orbital cohesive force includes an equally partitioned share of the nuclear repulsive force.

In an arbitrary molecule with n electrons, the orbital cohesive force can be defined in terms of a reference force given by

$$F^p_x(\mathrm{RF}) = -\frac{1}{n} F^p_x(\mathrm{NN}) \; . \tag{40}$$

However, in this case, the orbital forces would not all necessarily approach the same asymptotic limit.

Each of the orbital cohesive forces of paramagnetic N_2 is shown as a function of bond length in Fig. 5. The cohesive forces of the core $1\sigma_g$ and $1\sigma_u$ orbitals are observed to remain near zero but to become more bonding as the bond distance is decreased. That the core orbital cohesive forces are nonzero even at rather large internuclear separations appears surprising and suggests that the spherical symmetry of these orbitals about each site is being disturbed. We give evidence in Sec. III D that this effect is due to the core-penetration effects of the $3\sigma_g$ orbital.

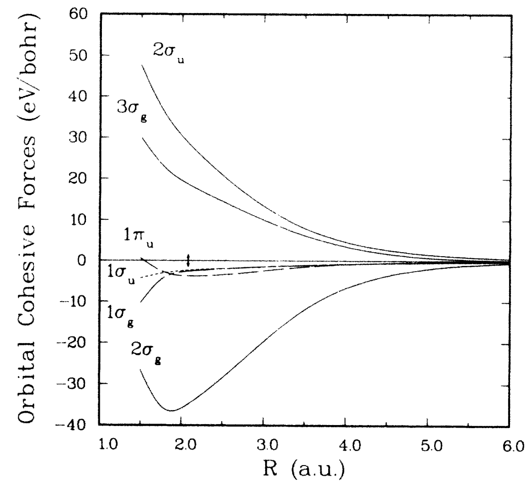

FIG. 5. Molecular-orbital cohesive forces, $F^p_{x,i}(c)$ [see Eq. (38)], in N_2 each as a function of the bond distance (R).

The $2\sigma_g$ and $1\pi_u$ cohesive forces go through minima at roughly the equilibrium separation of 2.08 bohr. Most of the chemical bond comes from the $2\sigma_g$ state, although the effect of the relatively weak $1\pi_u$ bond is amplified by its being occupied by four electrons. In this cohesive force picture, both the $2\sigma_u$ and $3\sigma_g$ states are antibonding.

The unexpected antibonding character of the $3\sigma_g$ state and the almost corelike behavior of the $1\pi_u$ state can be understood in terms of a near balance of orbital density forces from the charge density along the bond axis and the density in the regions "behind" the nuclei (Fig. 6).

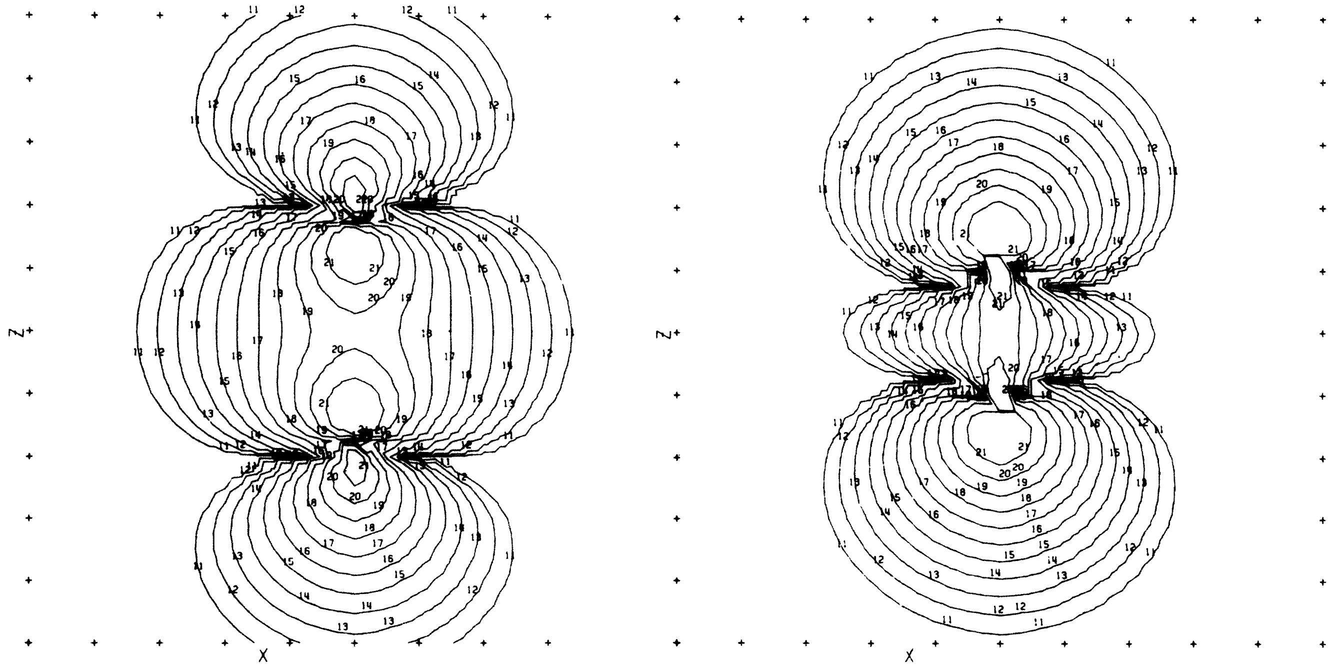

FIG. 6. Orbital charge density of the $3\sigma_g$ state in O_2 for elongated (left panel) and compressed (right panel) bond lengths showing charge shifts in the bond region. Adjacent density contours differ by a factor of 2.

TABLE III. Orbital reference forces (dimensionless) calculated in this work for the first-row homonuclear dimers (distance b in bohr; reference forces F(RF) in eV/bohr).

	b	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$\sum_i f_iF_i(\mathrm{RF})$	F(RF)
Li_2	5.10	0.22	0.25	−0.47					0.00	−1.57
Be_2	4.57	0.00	0.00	−1.54	1.54				0.00	−2.61
B_2	3.03	0.01	0.01	−1.41	1.43	−0.07[a]			−0.06	−7.41
C_2	2.36	0.01	0.01	−1.35	1.39	−0.04			0.00	−14.66
N_2	2.08	−0.12	−0.11	−1.58	1.30	−0.17	0.84		−0.02	−22.12
O_2	2.30	−0.17	−0.17	−2.05	1.33	−0.28	1.06	0.58[a]	0.04	−20.67
F_2	2.63	−0.17	−0.17	−1.89	1.00	−0.26	1.02	0.36	−0.02	−17.70

[a] These entries are for partially occupied states.

C. Static and dynamic descriptions of bonding

In the preceding section, the orbital cohesive force has been used to define and quantify the bonding or antibonding character of an orbital. If the force $F^p_{x,i}$ is more negative than the reference force [i.e., $F^p_{x,i}(C)<0$], the orbital is characterized as bonding. An orbital is considered antibonding if $F^p_{x,i}(C)>0$. This definition will be referred to as the static description of bonding and antibonding.

Another reasonable definition of bonding and antibonding can be obtained from the dynamic orbital force. A negative dynamic orbital force is characteristic of a bonding orbital, since it indicates that the bond length will increase when electronic charge is removed from this orbital. Conversely, an antibonding orbital will have a positive dynamic orbital force, i.e., bond contraction accompanies ionization from this type of state.

In Sec. III D, it will be seen that for the first-row dimers, the static and dynamic definitions of bonding and antibonding often agree in sign, although there are important exceptions. Tal and Katriel[8] have compared the two definitions in the Hartree-Fock theory and demonstrate that the dynamic definition is more closely related to the traditional concepts of bonding and antibonding introduced by Mulliken.[9]

D. Static orbital forces

In their study of the first-row dimers, Bader, Henneker, and Cade[4] (BHC) found it useful to divide out the explicit Z and b dependence of the orbital Hellmann-Feynman force. Their orbital force is given by (in a.u.)

$$F^p_{x,i}(\mathrm{BHC})=\frac{2b^2}{Z_p}F^p_{x,i}(\mathrm{HF}) . \tag{41}$$

We have also chosen to divide out the explicit Z and b dependence, but in a way which includes basis-set corrections and can be generalized to systems containing more than two atoms. We define a dimensionless orbital reference force given by

$$F^p_{x,i}(\mathrm{RF})=-\frac{F^p_{x,i}(C)}{F^p_x(\mathrm{RF})}=-\frac{[F^p_{x,i}-F^p_x(\mathrm{RF})]}{F^p_x(\mathrm{RF})} . \tag{42}$$

If the basis-set correction is ignored, the orbital force of BHC is related to this orbital reference force by the expression

$$F^p_{x,i}(\mathrm{RF})\approx 1-F^p_{x,i}(\mathrm{BHC}) . \tag{43}$$

Table III gives the orbital reference forces for the first-row dimers and can be compared with the reference forces of BHC reproduced in Table IV. Considering the differences in the basis sets and exchange-correlation models, the agreement of Tables III and IV is quite remarkable and indicates that the orbitals obtained in the two models are rather similar. The largest discrepancies occur for Be_2, and these are probably a consequence of the Hartree-Fock values being calculated for a bond distance where the force is nonvanishing.

Since the forces are evaluated near the equilibrium bond distances, the sum of the forces for each dimer (weighted by respective occupation numbers) should be approximately zero. Examination of Table III reveals that at equilibrium the orbital cohesive forces balance one another. For the dimers Li_2 through C_2, the orbital force picture is simple. The $1\sigma_g$, $1\sigma_u$, and $2\sigma_u$ orbital cohesive forces are positive and therefore antibonding, whereas the valence orbitals $2\sigma_g$ and $1\pi_u$ provide the necessary bonding charge to balance these repulsive forces. In Li^2, the large

TABLE IV. Reference orbital forces of Bader, Henneker, and Cade (Ref. 4) for the first-row homonuclear dimers.

	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$\sum_i f_iF_i(\mathrm{RF})$
Li_2	0.29	0.34	−0.59					0.08
Be_2	−0.05	−0.03	−1.00	1.40				0.64
B_2	0.02	0.03	−1.31	1.49	−0.19[a]			0.08
C_2	0.03	0.05	−1.25	1.44	−0.13			0.02
N_2	−0.16	−0.09	−1.68	1.46	−0.22	0.85		−0.12
O_2	−0.23	−0.14	−1.93	1.52	−0.30	0.83	0.57[a]	0.04
F_2	−0.24	−0.12	−1.45	1.17	−0.23	0.48	0.34	0.12

[a] These entries are for partially occupied states.

overlap charge of the $2\sigma_g$ orbital in the bond region polarizes the $1\sigma_g$ and $1\sigma_u$ states such that these core states are slightly antibonding. In Be_2, the $2\sigma_u$ orbital becomes occupied and, since the net density of the $2\sigma_g$ and $2\sigma_u$ states is nearly symmetrical about each site, there is little charge polarization of the $1\sigma_g$ and $1\sigma_u$ states. In B_2 and C_2, occupancy of the $1\pi_u$ orbital places charge in the off-axis bond region such that the core states become only very slightly antibonding.

In N_2, O_2, and F_2, the $3\sigma_g$ and $1\pi_g$ states become occupied. The characteristic charge accumulation in both binding and antibinding regions (the latter located behind each nucleus) for the $3\sigma_g$ state (Fig. 6) causes the $1\sigma_g$ and $1\sigma_u$ states to become polarized so that they exert attractive forces for the first time. The shorter bond length and a larger binding energy of N_2 compared with C_2 may appear surprising considering that it is the rather strongly antibonding $3\sigma_g$ orbital which becomes occupied in N_2. However, the increased attraction of the $1\pi_u$ and $2\sigma_g$ orbitals due to the increased nuclear charge more than makes up for the antibonding nature of the $3\sigma_g$ state.

Hirshfeld and Rzotkiewicz[25] ascribe the bonding character of the core orbitals in N_2, O_2, and F_2 to the large exchange field of the $3\sigma_g$ orbital near the nucleus. That the core polarization of these dimers comes from an indirect effect of the $3\sigma_g$ orbital can be demonstrated by calculating the orbital forces of ${N_2}^+$ and ${N_2}^{2+}$ such that the two electrons occupying the $3\sigma_g$ state in N_2 are successively removed. When one electron is removed from the $3\sigma_g$ state, the orbital forces of the $1\sigma_g$ and $1\sigma_u$ states are reduced by a factor of roughly 50%. Removal of the second electron from the $3\sigma_g$ state reduces the core polarization nearly to zero, thus verifying the indirect effect of the $3\sigma_g$ orbital on the bonding character of the core states.

E. Dynamic orbital forces

The dynamic orbital forces for the first-row dimers are given in Table V. In the dynamic force scheme, the core $1\sigma_g$ and $1\sigma_u$ orbitals are seen to be antibonding across the entire row with the forces of these orbitals obtaining maxima for N_2. Also in contrast to the static force description, the $3\sigma_g$ orbital is a bonding orbital in N_2, O_2, and F_2, although it is an unoccupied antibonding orbital in B_2 and C_2. These differences between the static and orbital forces reflect that they are really measures of different quantities. As in the static force picture, the strongest bonding orbital is the $2\sigma_g$ state.

The dynamic orbital forces provide an interesting description about the effects on bond length in response to changes in the orbital occupation numbers. From Eq. (27), if an infinitesimal (Δn) amount of charge is promoted from the ith to the jth orbital, the change in the total force (for constant bond distance) is

$$\Delta F_x^p = \left[\left[-\frac{\partial \varepsilon_j}{\partial X_p} \right] - \left[-\frac{\partial \varepsilon_i}{\partial X_p} \right] \right] \Delta n \; . \tag{44}$$

If the dynamic force of the jth orbital is greater than that of the ith orbital, the bond distance should be increased on charge transfer. Conversely, if the orbital force of the jth orbital is less than that of the ith orbital, the bond distance will be decreased.

This is illustrated in the case of the C_2 dimer. The four lowest multiplets of C_2 can be approximated[26] by the following set of occupation numbers: ${}^1\Sigma_g^+[1\pi_u(\uparrow\uparrow\downarrow\downarrow)]$, ${}^3\Pi_u[1\pi_u(\uparrow\uparrow\downarrow),3\sigma_g(\uparrow)]$, ${}^1\Pi_u[1\pi_u(\uparrow\uparrow\downarrow),3\sigma_g(\downarrow)]$, and ${}^3\Sigma_g^-[1\pi_u(\uparrow\uparrow),3\sigma_g(\uparrow\downarrow)]$. Since the repulsive force of the $3\sigma_g$ orbital is greater than the attractive force of the $1\pi_u$ orbital (see Table V), the bond distance of the multiplets should have the following order: ${}^1\Sigma_g^+ < {}^3\Pi_u \approx {}^1\Pi_u < {}^3\Sigma_g^-$. This prediction is in accord with both experiment[22] and theory.[21,26] In B_2, the $2\sigma_u$ orbital exerts a greater repulsive force than the $3\sigma_g$ orbital. Therefore, the ${}^3\Sigma_g^-$ multiplet $[2\sigma_u(\uparrow\downarrow),1\pi_u(\uparrow\uparrow)]$ should have a larger bond distance than the ${}^5\Sigma_g^-$ multiplet $[2\sigma_u(\uparrow),1\pi_u(\uparrow\uparrow),3\sigma_g(\uparrow)]$. Actual calculations verify this prediction also.[21]

Another inference from Table V that is substantiated both by calculation of the equilibrium bond length and/or by experiment[22] is that each of the lowest-energy states of the ions ${B_2}^+$, ${C_2}^+$, and ${N_2}^+$ should have a larger bond distance than its corresponding neutral partner (B_2, C_2, or N_2). Also consistent with experiment, the dynamic orbital forces predict that ${O_2}^+$ and ${F_2}^+$ should have smaller bond distances than O_2 and F_2.

The dynamic orbital forces reported by Tal and Katriel[8] as computed within the Hartree-Fock model are given in Table VI. The signs of the Hartree-Fock forces are the same as those in Table V, but their magnitudes are, with a few exceptions, very different. The difference in the forces in the two tables is likely a consequence of a fundamental difference between Hartree-Fock one-electron energies and those obtained in the LSDA, i.e., the Hartree-Fock one-electron energies satisfy Koopman's theorem,

TABLE V. Density-functional dynamic orbital forces (in eV/bohr). The energies correspond to occupied orbitals unless indicated otherwise.

	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$3\sigma_u$
Li_2	0.25	0.27	−0.11					
Be_2	0.26	0.26	−0.82	0.40				
B_2	1.45	1.51	−1.77	1.18	−1.21[a]	0.04[b]		
C_2	3.31	3.51	−3.04	2.44	−1.82	0.26[b]		
N_2	3.86	4.07	−7.65	3.75	−4.15	−0.38	6.52[b]	
O_2	1.54	1.55	−11.23	4.34	−4.62	−0.98	4.44[a]	
F_2	0.82	0.83	−7.45	3.70	−2.87	−1.95	2.39	9.6040[b]

[a] These entries are for partially occupied orbitals.

[b] Energies correspond to unoccupied orbitals.

TABLE VI. Hartree-Fock dynamic orbital forces (in eV/bohr), from Tal and Katriel (Ref. 8).

	$1\sigma_g$	$1\sigma_u$	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$
Li_2	0.08	0.11	−0.26				
Be_2							
B_2	0.93	1.01	−2.72	1.93	−2.10[a]		
C_2	4.00	4.24	−5.03	3.84	−3.43		
N_2	3.56	4.05	−11.51	3.95	−7.18	−2.33	
O_2	2.45		−13.96	5.41	−6.07	−3.73	5.31[a]
F_2							

[a] These entries are for partially occupied states.

whereas the one-electron energies of the LSDA, in general, do not.[27] Since the one-electron energies in the two models are related in different ways to the total energy, their derivatives with respect to bond distances reflect these differences.

IV. CONCLUSION

Analysis of static orbital forces in the first-row dimers has been shown to provide useful insight into the roles played by the different orbitals in chemical bond formation. The good agreement of the static forces with those obtained in the Hartree-Fock model suggests that a static orbital force analysis will be somewhat invariant to the exchange-correlation model that is used.

Although they are more sensitive to the exchange-correlation potential, the dynamic orbital forces are relatively easy to obtain. All that must be computed is the set of ε_i for several internuclear separations and from this the numerical derivative $-\partial\varepsilon_i/\partial X_p$ can be determined. A high degree of self-consistency is required in order to obtain highly accurate dynamic forces, but qualitative analysis of ionized and excited states of molecules should be possible with only moderately converged results.

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[1] J. O. Hirschfelder and W. J. Meath, Adv. Chem. Phys. **12**, 3 (1967).

[2] J. C. Slater, J. Chem. Phys. **57**, 2389 (1972).

[3] L. J. Sham, Phys. Rev. B **32**, 3876 (1985), and references therein.

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

[5] F. W. Averill and G. S. Painter, Phys. Rev. B **32**, 2141 (1985).

[6] P. E. Cade, R. F. W. Bader, W. H. Henneker, and I. Keaveny, J. Chem. Phys. **50**, 5313 (1969).

[7] R. F. W. Bader, in *The Force Concept in Chemistry*, edited by B. M. Deb (Van Nostrand Reinhold, New York, 1981).

[8] Y. Tal and J. Katriel, Theoret. Chim. Acta (Berlin) **46**, 173 (1977).

[9] R. S. Mulliken, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. O. Lowdin (Academic, New York, 1966).

[10] J. C. Slater, *Quantum Theory of Molecules, and Solids* (McGraw-Hill, New York, 1974), Vol. 4.

[11] J. F. Janak, Phys. Rev. B **18**, 7165 (1978); see also J. P. Perdew, R. G. Parr, M. Levy, and J. L. Balduz, Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[12] C. Satoko, Phys. Rev. B **30**, 1754 (1984).

[13] P. Bendt and A. Zunger, Phys. Rev. Lett. **50**, 1684 (1983).

[14] This expression without the basis-set correction term was previously obtained by Tal and Katriel (Ref. 8) in the Hartree-Fock model.

[15] This assumption can be easily proven by making use of the fact that in density-functional theory, the total energy is a functional of the density, $\rho(\mathbf{r})$.

[16] The description, "unconstrained," is somewhat misleading in that the orbitals $\psi_i(\mathbf{r})$ are still required to be eigenfunctions of $H(\mathbf{r})$ during the differentiation. Consequently, the so-called unconstrained orbitals are not completely free during the differentiation process.

[17] G. S. Painter and F. W. Averill, Phys. Rev. B **28**, 5536 (1983).

[18] S. H.Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[19] G. S. Painter, Phys. Rev. B **24**, 4264 (1981).

[20] F. B. van Duijneveldt, IBM Research Report No. RJ945, 1971 (unpublished).

[21] G. S. Painter and F. W. Averill, Phys. Rev. B **26**, 1781 (1982).

[22] K. P. Huber and G. L. Herzberg, *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), Vol. IV.

[23] V. E. Bondybey and J. H. English, J. Chem. Phys. **80**, 568 (1984).

[24] The basis-set corrections, $F^{p}_{x,i}$(BS), are mathematical artifacts of the basis set and have no physical meaning.

[25] F. L. Hirshfeld and S. Rzotkiewicz, Mol. Phys. **27**, 1319 (1974).

[26] O. Gunnarsson, J. Harris, and R. O. Jones, J. Chem. Phys. **67**, 3970 (1977).

[27] This difference in one-electron energies is discussed in detail by J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).