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Orbital forces in the density-functional formalism: Application to the copper dimer

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The force field in an atomic cluster, given as the direct gradient of the total energy in the density-functional formalism, is expressed in terms of components corresponding to the solutions of the one-particle Schrödinger equation. The resulting relationship between eigenfunctions and orbital forces provides a useful framework for analysis of the bonding in the system. The expression for the orbital force is given as the sum of a traditional Hellmann-Feynman term and an orbital derivative term which cancels the first-order error due to basis-set incompleteness. The sum of orbital forces gives the total gradient force on the nuclei in the system to essentially the same accuracy as the total-energy surface itself. Results are reported for an all-electron calculation of the orbital forces in the copper dimer. This first local-spin-density calculation of the gradient force for a transition-metal dimer represents a challenging test because of the heavy core. By the introduction of a simple screening force, an orbital cohesive force is defined which provides an interesting and useful framework for quantifying the relative contribution of the molecular orbitals to the chemical bond. The effects of core polarization and valence hybridization and their compensating influence are demonstrated in the results.

I. INTRODUCTION

The Hellmann-Feynman theorem[1,2] states that the exact force experienced by a particular nucleus in a cluster of atoms 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. It has long been recognized that the practical utility of this theorem is very limited by the requirement of exact wave functions for its validity. At the same time, the theorem does afford an interesting conceptual basis for analysis of the bonding in systems. A force can be calculated according to the theorem, with an accuracy which will depend on the (first-order) basis-set error. The x component of this Hellmann-Feynman force (on the pth nucleus) is expressed in atomic units as

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

This force, though formally the same as that which would be obtained as the negative gradient of the total-energy hypersurface, is never numerically the same except for an extremely accurate self-consistent density. Calculations of the Hellmann-Feynman force have been of limited value for the basis sets typically used in most calculations. This limitation has been addressed by workers carrying out *ab initio* and Hartree-Fock molecular calculations for some time, and ways have been developed to include corrections to the Hellmann-Feynman force field through energy-gradient techniques.[3] Theoretical studies of potential surfaces have been advanced by the development of techniques to evaluate analytic derivatives for general-type wave functions.[4]

More recently, these energy-gradient concepts have been developed within the density-functional formalism using the local-spin-density approximation (LSDA). Satoko[5] presented a method for evaluating the energy gradient (with respect to atomic coordinates) in the linear combination of atomic orbitals (LCAO) $X\alpha$ approach and applied it to a cluster model of an oxygen atom chemisorbed on the Al(111) surface. Generalized force formulas and further applications have recently been presented.[6] A formalism for direct calculation of the force has also been independently derived within the density-functional approach by Bendt and Zunger.[7] In other LSDA works, adequate Hellmann-Feynman forces have been obtained for light molecules through the use of accurate basis sets,[8] in some cases combined with circumvention of the special problem of the core, either by a valence-only energy-functional approach[9] or by pseudopotential methods.[10]

The basic idea in these recent developments is the direct evaluation of the gradient of the total energy with respect to the specified nuclear coordinate, allowing for the implicit dependence of the one-electron wave functions on the nuclear coordinate, which arises for nuclear site-centered functions. The force is then easily shown to be[6,7] the usual Hellmann-Feynman component plus an additional basis derivative force term; for example, the x component is written (in the following, the force will be understood to be that on the pth nucleus)

$$\begin{aligned} F_x^p &\equiv -\frac{\partial E}{\partial X_p} \\ &= F_x^p(\mathrm{HF}) - \left[\sum_i f_i \int \frac{\partial \psi_i^*(\mathbf{r})}{\partial X_p} H(\mathbf{r}) \psi_i(\mathbf{r}) d\mathbf{r} + \text{c.c.} \right] . \end{aligned} \quad (2)$$

The second term in Eq. (2) corrects the Hellmann-Feynman force for basis set incompleteness in the sense that the first-order basis-set error is canceled.[11] This corrective term then puts the force on the same footing regarding approximations as the total energy.

In the derivation of Satoko[6] a decomposition of the total gradient force into pair interaction forces between atoms is introduced corresponding to an atomic partitioning of the electron charge density according to a Mulliken population analysis. This decomposition of the total force provides a useful way of analyzing the bonding in the system. In the following, we describe a simple alternate way of analysis of the total force which establishes a connection with the single-particle solutions of the Schrödinger equation. The total force due to the electron density is decomposed into molecular-orbital (eigenfunction) constituents. Carrying out such an analysis with the Hellmann-Feynman term alone has been found to provide useful insight into the nature of bonding in transition-metal dimers.[12] In the following, this orbital force description is developed within the gradient approach, such that the total force obtained on summation over occupied states is of the same accuracy as the negative derivative of the total-energy surface.

II. ORBITAL FORCES IN THE ENERGY-GRADIENT APPROACH

In the density-functional formalism,[13,14] the minimization of the total energy (corresponding to determination of the ground-state density ρ and energy E) is shown to be equivalent to the self-consistent solution of a set of one-electron equations,

$$H(\mathbf{r})\psi_i(\mathbf{r})=\epsilon_i\psi_i(\mathbf{r}) \ , \tag{3}$$

where the corresponding density is given by

$$\rho(\mathbf{r})=\sum_i f_i \, |\psi_i(\mathbf{r})|^2 \tag{4}$$

with occupation numbers f_i corresponding to the orbital solutions ψ_i.

Since the electronic part of the Hellmann-Feynman force depends on the density linearly, it can be expressed as a sum of *orbital forces*.[15] The x component of the Hellmann-Feynman orbital force for state "i" is defined as

$$F^{p}_{x,i}(\mathrm{HF})\equiv \int |\psi_i(\mathbf{r})|^2 \frac{\partial}{\partial X_p}\left[\frac{Z_p}{|\mathbf{r}-\mathbf{R}_p|}\right] d\mathbf{r} \ . \tag{5}$$

The same orbital decomposition carries over to the total force calculated by the gradient method. In this case, however, new terms enter in addition to the orbital Hellmann-Feynman terms of Eq. (5) due to the implicit dependence of the orbitals on nuclear position:[6,7]

$$F^{p}_{x,i}(\mathrm{BS})\equiv -\left[\int \frac{\partial\psi_i^*(\mathbf{r})}{\partial X_p} H(\mathbf{r})\psi_i(\mathbf{r}) d\mathbf{r}+\text{c.c.}\right] . \tag{6}$$

These terms cancel the first-order error in the orbital Hellmann-Feynman force so that basis set sensitivity is greatly reduced. The net x component of the (ith) orbital force is then simply

$$F^{p}_{x,i}\equiv F^{p}_{x,i}(\mathrm{HF})+F^{p}_{x,i}(\mathrm{BS}) \ . \tag{7}$$

The gradient force is then expressed in terms of the orbital forces as

$$-\frac{\partial E}{\partial X_p}=\sum_i f_i F^{p}_{x,i}+F^{p}_{x}(\mathrm{NN}) \ , \tag{8}$$

where

$$F^{p}_{x}(\mathrm{N})\equiv -\sum_{q\,(\neq p)} \frac{\partial}{\partial X_p}\left[\frac{Z_p Z_q}{|\mathbf{R}_p-\mathbf{R}_q|}\right] \tag{9}$$

is the repulsive nuclear component. The gradient force, Eq. (8), is equivalent to the negative derivative of the total-energy hypersurface at a prescribed location in the parameter space, showing relatively the same sensitivity to basis-set choice as the total energy itself.

For linear variational calculations utilizing a fixed basis set, Eq. (6) can be put into a more computationally convenient form. The orbital solutions are expanded as linear combinations of basis functions $\chi_i(\mathbf{r})$,

$$\psi_i(\mathbf{r})=\sum_j C^i_j \chi_j(\mathbf{r}) \ . \tag{10}$$

The orbital derivative (with respect to nuclear coordinate) in Eq. (6) then resolves into two derivatives, one of the basis functions, the other of the coefficients $\{C^i_j\}$. The site dependence in most basis functions is such that the first-type derivatives are straightforward to evaluate. Differentiation of the coefficients is conveniently handled since, as demonstrated by Pulay,[3] they can also be expressed in terms of derivatives of the basis functions. The correction term to the ith orbital force then takes the form

$$F^{p}_{x,i}(\mathrm{BS})=-\sum_{j,k} C^{i*}_j C^i_k \int \frac{\partial \chi_j^*}{\partial X_p}[H(\mathbf{r})-\epsilon_i]\chi_k(\mathbf{r}) d\mathbf{r}+\text{c.c.} \ , \tag{11}$$

which can be compared with the derivations of the correction to the total force of Satoko[6] and of Bendt and Zunger[7] when summed over occupied states.

In the calculations for the copper dimer which are described in the following, orbital and total gradient forces are used to analyze the stability of the molecule. The accuracy of the gradient force is demonstrated by comparison of the total force curve calculated using Eq. (8) with the negative energy derivative calculated numerically from the binding energy curve.

III. FORCES IN THE COPPER DIMER

Calculation of the orbital forces for the copper dimer has been carried out as an extension of the augmented Gaussian orbital linear variational method which has been described previously.[16] Evaluation of the Hellmann-Feynman orbital forces according to Eq. (5) is carried out analytically using the algorithms of McMurchie and Davidson.[17] Many of the integrals involved in the computation of the corrective terms to the orbital force in Eq. (11) are also evaluated analytically. Exceptions are the integrals over the Coulomb and exchange-correlation potentials, which are evaluated by the same numerical techniques described for the corresponding matrix elements in the augmented Gaussian orbital approach.[16]

There is no restriction to a particular type of exchange-correlation potential in this approach, but for continuity with our earlier published study of Cu_2, only results from the $X\alpha$ (with exchange factor $\alpha=0.7$) model will be presented here.[18] Two basis sets were used in these calculations—one derived from the minimum [14*s*, 11*p*, 5*d*/4*s*, 2*p*, 1*d*] Gaussian basis,[19] the other an extended basis [14*s*, 11*p*, 5*d*/6*s*, 4*p*, 3*d*] generated by adding the two most diffuse Gaussians in the *s*, *p*, and *d* channels.[16]

A. Total force in Cu_2

The total force on one of the copper nuclei is plotted as a function of internuclear separation in Figs. 1(a) and 1(b) for the minimum and extended basis sets, respectively. The force has been calculated by the gradient method using Eq. (8). Also appearing in Fig. 1 are force values (triangles) calculated by direct numerical differentiation of the total-energy curves. The agreement between the gradient and numerical force values provides a stringent cross-check of the internal consistency of the energy and force calculational procedures and establishes the convergence properties of the gradient approach.

Vanishing of the force on the nuclei occurs at approximately 4.22 a.u. with the minimum basis compared with a value of approximately 4.13 a.u. for the extended basis. These equilibrium bond lengths are consistent with our previously published results,[16] with the extended basis bond length contracted about 2% relative to the experimental value[20] of 4.20 a.u.

The striking similarity between the gradient-force curves of Fig. 1 for these two different basis sets attests to the removal of first-order basis-set errors in the Hellmann-Feynman force through the correction terms. The total gradient force calculated by Eq. (8) is, in this case, highly insensitive to basis choice. The gradient-force curve for the extended basis is to a very good approximation simply a rigid displacement of that for the minimal basis, consistent with the change observed in the binding energy curve.

On the other hand, the uncorrected Hellmann-Feynman force curves with both basis sets are in large error for all separations, becoming repulsive only for very contracted bond lengths. The Hellmann-Feynman force curve for the extended basis is shown in Fig. 2. At the equilibrium separation, the uncorrected Hellmann-Feynman force lies off the scale of the gradient-force curves in Fig. 1 by factors of 4 and 12 for the minimum and extended basis-set results, respectively.

B. Orbital forces in Cu_2

In Table I, the orbital forces for all occupied states in Cu_2 are given for the extended basis calculation with a fixed bond length of 4.1 a.u. For each state of specified symmetry in column 1, the occupation number (weight for the orbital force), Hellmann-Feynman force (in eV/bohr) as given by Eq. (5), basis-set correction term [Eq. (6)], orbital force [Eq. (7)], and orbital force weighted by the number of electrons appear in columns 2 through 6. Discussion of the entries in columns 7 and 8 will be deferred to the next section. The values of F_i(HF) fall in a

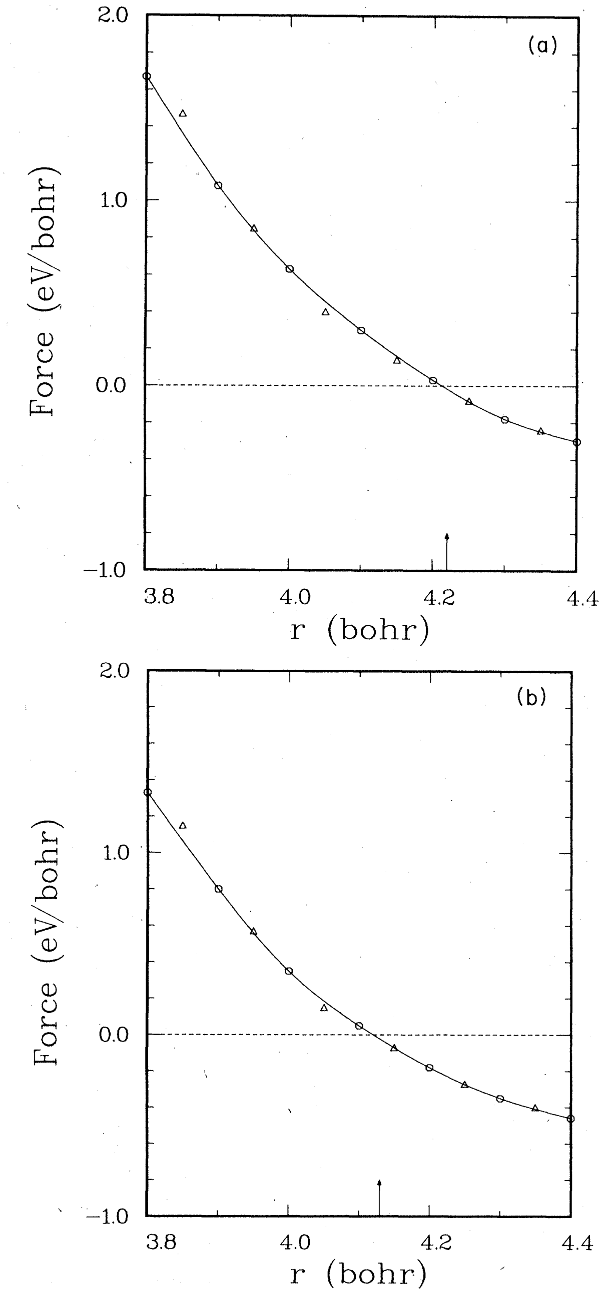

FIG. 1. Cu_2 total gradient force (in eV/bohr) as a function of the bond distance, *r*, for the (a) minimal basis set and (b) extended basis set. The force is computed both as a simple numerical derivative of the binding energy curve (triangles) and as the sum of the orbital forces (circles) from Eq. (8). Equilibrium position as determined from minimum in binding energy curve denoted by vector on axis.

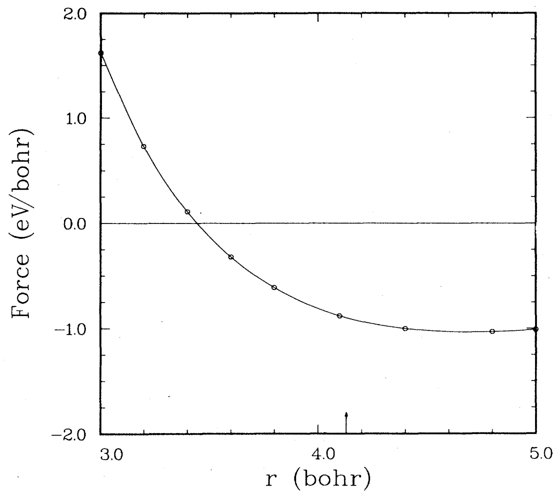

FIG. 2. Total Hellmann-Feynman force (in eV/bohr) in Cu_2 as a function of internuclear separation r (in bohr) for extended basis set. Vector on axis denotes equilibrium separation (zero force) according to binding energy minimum and zero gradient force.

rather narrow band at approximately −23 eV/bohr. The orbital exhibiting the greatest attractive force is the $6\sigma_g$ as expected, and it is for this orbital that the basis-set correction, F_i(BS), is greatest. It is observed that with the exception of the lowest two valence states, the basis-set corrections are all near zero or positive for all states, consistent with the result that the total Hellmann-Feynman force is much too attractive at this bond length. The negative values for F_i(BS) for the $6\sigma_g$ and $3\pi_u$ bonding states signify that the orbital densities of these states are not sufficiently well converged (in basis) to provide the degree of attractive force consistent with the energy curve.

This is further evidenced in comparison of the results for minimum and extended basis sets where the orbital forces of the $6\sigma_g$ and $3\pi_u$ states are more attractive (as are those of all the valence levels) for the extended basis. The basis-corrective terms F_i(BS), while still negative, are smaller in magnitude for the extended basis than are those for the minimum basis. For nearly all of the other states, the basis-set corrections F_i(BS) (all positive) are greater than those for the minimum basis set. This seems curious at first sight, but is consistent with a lower-lying Hellmann-Feynman force curve for the extended basis at this separation. The basis-set extension, while bound to give a lower energy by the variation principle, is not guaranteed to provide uniform convergence of the Hellmann-Feynman force to the exact force. The higher-lying $3\pi_g$ and $6\sigma_u$ antibonding levels are observed to become more attractive on basis extension, signifying a need for additional basis functions to span the antibonding states for an improved Hellmann-Feynman force. It is interesting to observe the effects of basis extension reflected in appreciable changes in the core region; for example, a reduced attraction of the 4σ (predominantly $3s$-like) orbital forces accompanies the enhanced attraction associated with the 6σ and 5σ orbitals.

The total force obtained by summing the orbital contri-

TABLE I. Orbital forces in units of eV/bohr for Cu_2 at $b=4.1$ bohr with extended basis. The orbital Hellmann-Feynman force, F_i(HF), is corrected by the orbital derivative term, F_i(BS), to give the gradient orbital force F_i. The orbital cohesive force, $F_i(C)$, results by subtraction of the point-charge reference force (−23.47 eV/bohr) from F_i. Occupation numbers f_i denote state population.

State	f_i	F_i(HF)	F_i(BS)	F_i	f_iF_i	$F_i(C)$	$f_iF_i(C)$
				Core			
$1\sigma_g$	2	−23.14	0.71	−22.45	−44.89	1.03	2.05
$1\sigma_u$	2	−23.22	0.79	−22.45	−44.89	1.02	2.05
$2\sigma_g$	2	−20.87	0.35	−20.52	−41.04	2.95	5.90
$2\sigma_u$	2	−20.64	0.13	−20.53	−41.05	2.95	5.89
$3\sigma_g$	2	−26.19	0.79	−25.38	−50.77	−1.91	−3.82
$3\sigma_u$	2	−26.12	0.72	−25.39	−50.77	−1.91	−3.83
$1\pi_u$	4	−23.24	0.56	−22.68	−90.72	0.79	3.17
$1\pi_g$	4	−23.24	0.56	−22.68	−90.73	0.79	3.16
$4\sigma_g$	2	−18.14	0.14	−18.00	−36.00	5.47	10.95
$4\sigma_u$	2	−17.48	0.09	−17.39	−34.79	6.08	12.16
$5\sigma_g$	2	−28.33	0.16	−28.17	−56.34	−4.70	−9.40
$5\sigma_u$	2	−28.67	0.22	−28.44	−56.88	−4.97	−9.93
$2\pi_u$	4	−21.33	0.15	−21.19	−84.77	2.28	9.12
$2\pi_g$	4	−21.08	0.12	−20.96	−83.86	2.51	10.03
				Valence			
$6\sigma_g$	2	−36.21	−0.65	−36.85	−73.71	−13.38	−26.76
$3\pi_u$	4	−25.99	−0.11	−26.09	−104.35	−2.61	−10.46
$1\delta_g$	4	−22.35	0.29	−22.08	−88.31	1.40	5.58
$7\sigma_g$	2	−26.63	0.41	−26.22	−52.45	−2.75	−5.50
$1\delta_u$	4	−21.39	0.48	−20.92	−83.63	2.56	10.26
$3\pi_g$	4	−25.75	1.33	−24.43	−97.67	−0.95	−3.78
$6\sigma_u$	2	−28.35	1.49	−26.87	−53.72	−3.39	−6.77

butions of Hellmann-Feynman and basis-set correction origin is given with the total orbital force and nuclear-nuclear repulsive term in Table II. The necessity of the basis-set corrections for an accurate total force is clear from these results. Errors in the Hellmann-Feynman force alone amount to 8 and 24 eV/bohr for the minimum and extended basis sets, respectively. While these are errors of only approximately 1% to 2%, the components of the total force are each four orders of magnitude greater than their sum, so that structure determinations would be in large error without the corrective terms of the gradient force.

C. Orbital cohesive forces in Cu_2

A striking feature of Table I is that the orbital force of the different states, F_i, varies over a narrow range; most forces fall between -20 and -25 eV/bohr. This characteristic can be easily understood in terms of a simple screening model. If an electron's charge in the copper dimer were distributed in localized spherically symmetric charge distributions centered on the two nuclei, the electrostatic force of that electron's charge on a given nucleus would be due entirely to the charge distribution centered on the other site. The charge of that distribution would be[21] $e/2$ and the electrostatic force due to that distribution on the nucleus would be $-Ze^2/2b^2$ where in atomic units $e=1$, and for the copper reference system $Z=29$ and $b=4.1$ bohr. This gives a force of -0.86 hartree/bohr or -23.47 eV/bohr, which is about the midpoint of the range of forces in Table I.

As a first approximation then, the orbital force is given by simple equipartitioning of the orbital charge into fractional point charges on the atomic sites. This value for the orbital force is also the limiting value on separation of the nuclei such that the bonding between sites vanishes and the molecular orbitals are sums of nonhybridizing atomic orbitals. From this standpoint, the point-charge-model force represents a useful reference *nonbonding* force value by which the bond character of the orbitals can be quantified. From another point of view, this reference value is the portion of internuclear repulsive force which each orbital would have to balance, if all orbitals were equivalent, in order that the sum of orbital and internuclear forces vanish.

Of course, the orbitals are not all equivalent and some contribute more strongly to bonding than others. The orbital forces of Table I are observed to fall nearly equally about the reference value, suggesting the qualitative one-electron bonding picture of some orbitals which effect cohesion and others which do not contribute significantly to cancellation of the nuclear repulsion. Those orbitals giving forces which are appreciably larger in magnitude than the reference value are associated with bonding orbitals. Other orbitals showing forces much reduced from the reference are suggestive of antibonding (since they do not effect complete cancellation of the portion of the nuclear repulsion associated with one electron). Orbitals with forces near the reference value are characterized as nonbonding.

The relative differences in bonding character of the various orbitals can be emphasized by subtraction of the reference force from each orbital force, F_i:

$$F_i(c) \equiv F_i + Ze^2/2b^2 \ . \tag{12}$$

This new force is a direct measure of how effectively the orbital binds the nuclei together in the molecule. For this reason, it will be referred to as an *orbital cohesive force.* The sign of the orbital cohesive force indicates the nature of the bond character (bonding or antibonding) of the relevant state. Another useful property of the orbital cohesive forces in that the sum over occupied states in the dimer gives (with $2Z$ electrons in the system) a net cohesive force,

$$\begin{aligned}\sum_i f_i F_i(c) &= \sum_i f_i F_i + (2Z)(Ze^2/2b^2) \\ &= \sum_i f_i F_i + Z^2e^2/b^2 \ .\end{aligned} \tag{13}$$

The second term in Eq. (13) is simply the nuclear repulsive force so that

$$\sum_i f_i F_i(c) = \sum_i f_i F_i + F(\mathrm{NN}) \ . \tag{14}$$

The right-hand side of Eq. (14) is, from Eq. (8), $-\partial E/\partial X$, i.e., the orbital cohesive forces summed over all states give the total gradient force on the nucleus.[22]

The calculated orbital cohesive forces (and occupation number weighted values) are given in columns 7 and 8 of Table I, and the results clearly delineate the effective bonding and antibonding states. Those orbitals giving negative cohesive forces are effectively shielding the point charge defining the reference force while those characterized by positive values are incompletely shielding this unit internuclear repulsion. These orbital cohesive forces will be used in the next section to analyze the bonding in the copper dimer.

TABLE II. Components of the total gradient force in Cu_2 at the reference bond length of $b=4.1$ a.u. Orbital components are defined in the text and given in Tables I and II. The basis derivative terms, $F_i(\mathrm{BS})$, correct the Hellmann-Feynman terms, $F_i(\mathrm{HF})$, to give the orbital forces, F_i. The sum over the latter combines with the nuclear-nuclear repulsion, $F(\mathrm{NN})$, to give the total force, $-\partial E/\partial X$. Units are in eV/bohr.

	$\sum_i f_i F_i(\mathrm{HF})$	$\sum_i f_i F_i(\mathrm{BS})$	$\sum_i f_i F_i$	$F(\mathrm{NN})$	$-\partial E/\partial X$
Minimum basis	-1369.0878	$+8.0005$	-1361.0873	$+1361.3918$	$+0.3045$
Extended basis	-1385.2120	$+23.8959$	-1361.3161	$+1361.3918$	$+0.0757$

D. Bond analysis for Cu_2

In an earlier study of bonding in the copper dimer[16] the Hellmann-Feynman valence orbital forces were found to be attractive at equilibrium separation and to fall in a range of about -1.5 to -2.7 hartree/bohr (including the occupation number weight factor). The orbital cohesive forces calculated within this gradient approach provide greater detail on the nature of bonding in Cu_2.

The largest attractive (negative) orbital cohesive force is given by the $6\sigma_g$ state, and the $3\pi_u$ orbitals are observed to provide a strong attraction when weighted by the four electrons occupying these degenerate levels (Table I). Bonding in Cu_2 is clearly dominated by s-s and $d\sigma$-$d\sigma$ hybridized orbitals with a secondary but significant $d\pi$-$d\pi$ component. The $d\delta$-$d\delta$ contributions emerge as weakly antibonding for both $1\delta_g$ and $1\delta_u$ orbitals.

It may at first sight appear curious that the $1\delta_g$ orbital which is traditionally viewed as "bonding" gives a repulsive orbital cohesive force. But examination of the orbital density [Fig. 7(a) in Ref. 16] shows the charge distributed in lobes perpendicular to the bond axis, and this results in an insufficient cancellation of the repulsive point-charge reference force which defines net bonding behavior. Similarly, the $3\pi_g$ and $6\sigma_u$ orbitals, normally viewed as antibonding, can give negative orbital cohesive forces (attractive) depending upon the relative amounts of density shifted from the bond region to the space outside the bond.[23] Near equilibrium in the copper dimer, these states might best be viewed as nonbonding since their orbital forces are never very strong and can change from attractive to repulsive with small changes in bond length and basis set.

One of the more striking features to emerge from the calculation of the orbital cohesive forces is the clear importance of the core states ($1\sigma_g$ through $2\pi_g$ in Table I). Not only are the magnitudes of these forces appreciable, but a distribution among attractive and repulsive types is also apparent. The importance of core polarization is quite clear from these results, for if the core orbitals were actually unaltered from the atom, they would be characterized by vanishing orbital cohesive forces.

The role of the core electrons is further illustrated in the results summarized in Table III, where the atomic parentage of the various core and valence molecular orbitals is shown. Partial sums over the core orbital cohesive forces by atomic shell show that those of p-type atomic origin are individually large (Table I) but largely cancel within the shell (Table III). The remaining orbital cohesive forces of s-type origin combine to give a large net repulsive core force, which, at the energy minimum, exactly balances the large attractive force produced by the sum over valence orbital cohesive forces.[24] The characteristic that the sum over core orbital cohesive forces defines a net repulsive force while that for the valence orbitals is attractive is quite general.[25] The defined orbital cohesive force thus serves to identify the nature of the bonding in the dimer in terms of a balance between repulsive and attractive forces originating in the core and valence space, respectively. It is clear from the results that a frozen-core approximation would produce a very inaccurate total force without corrections to account for core polarization.[26,27]

TABLE III. Orbital cohesive force partial sums for bound molecular orbitals (MO) of various atomic orbital (AO) parentage for Cu_2. The sum, $\sum''$, is over states within the given atom core shell; $\sum'$ includes all core and valence separately, and $\sum$ includes all states. Values of $F_i(C)$ from Table I; units are in eV/bohr.

AO	MO	$\sum''_i f_iF_i(C)$	$\sum'_i f_iF_i(C)$	$\sum_i f_iF_i(C)$
1s	$1\sigma_g$ $1\sigma_u$	4.10	37.50	+0.07
2s	$2\sigma_g$ $2\sigma_u$	11.79		
2p	$3\sigma_g$ $3\sigma_u$ $1\pi_u$ $1\pi_g$	-1.32		
3s	$4\sigma_g$ $4\sigma_u$	23.11		
3p	$5\sigma_g$ $5\sigma_u$ $2\pi_u$ $2\pi_g$	-0.18		
3d,4s	$6\sigma_g$ $3\pi_u$ $1\delta_g$ $1\delta_u$ $3\pi_g$ $6\sigma_u$		-37.43	

IV. SUMMARY

Energy-gradient techniques have been used to derive one-electron orbital forces within the density-functional formalism. The sum of these forces is equivalent to the negative of the direct derivative of the total-energy hypersurface at the relevant point in parameter space. Accounting for the implicit dependence of the basis orbitals of nuclear coordinates removes the first-order error due to basis incompleteness and determines the gradient force to the same level of accuracy as the energy. Although not an extremal quantity like the energy, the force requires only a few further iterations beyond that required for the energy to establish convergence adequate for mapping the energy surface. Knowledge of the force field in a cluster is of crucial importance as the number of atoms N is increased. Explicit evaluation of the energy in the $3N$ parameter space of nuclear positions is reduced by a factor of order $3N$ for arbitrary geometries when the forces on the nuclei are known.

The individual orbital forces corresponding to the solutions of the local-spin-density equations provide further insight into the bonding mechanisms in the cluster. By introducing a point-charge electrostatic reference force representing the portion of nuclear charge which must be shielded by a given orbital in order for a net attraction to occur through occupation of the state, an orbital cohesive force has been defined whose sign alone signifies the type contribution made to stability of the cluster.

In an application to the copper dimer, the utility of the gradient approach in treating transition-metal clusters has been demonstrated by the excellent correspondence between the gradient force and the direct numerical derivative of the energy curve. The necessity of the basis-set corrective terms to the usual Hellmann-Feynman force was shown to be crucial for Cu_2.

The orbital forces for Cu_2 show the major role of s-s and $d\sigma$-$d\sigma$ bonding with significant components in the $d\pi$-$d\pi$ mode. The orbital forces of the δ states were identified as repulsive, and this characteristic was attributed to the orientation of the δ bonds relative to the dimer axis. The results for Cu_2 clearly identify the nature of the core polarization which accompanies bonding in the valence space. The core-electron distribution is altered by the valence bonding such that each core electron no longer completely shields a proton in the nucleus. The p-core electrons give both attractive and repulsive cohesive forces, however, the π and σ components largely cancel such that almost the entire core cohesive force is due to the s-core states, each characterized by a repulsive cohesive force. The net repulsive core cohesive force is balanced by the attractive valence cohesive force at equilibrium. From this point of view, the valence orbitals are very effective in giving a net attractive force, and it is only the diminishing of the core orbital forces through polarization and commensurate net core repulsion that equilibrium results.

While the orbital forces F_i and orbital cohesive forces $F_i(C)$ are useful conceptually, their individual numeric values are much more basis set dependent than their sum. Their relative values are rather invariant to basis set, however, and this affords the framework used in this work for interpretation of the bonding in Cu_2. Another point concerning the orbital forces is that their connection with the respective orbital charge densities is not direct except in the case of exact solutions. This is not a problem in typical uses of the orbital densities, such as interpretation of the bonding. It should be kept in mind, however, that while the Hellmann-Feynman orbital force is based on orbital density alone, the basis derivative corrections bring in less interpretable contributions arising from the integrals of the orbital derivatives and Hamiltonian, e.g., kinetic-energy and exchange-correlation terms.

The availability of accurate force fields for atomic clusters is opening whole new classes of problems for study, both through reduction in calculational effort and through enhanced conceptual insight offered in the results. The present contribution extends the gradient approach in the density-functional formalism to the important class of transition-metal atomic clusters. It is anticipated that the new information available in the orbital forces can be used to gain further insight into the one-electron characteristics of bonding and interactions in atomic clusters.

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[22] While this model is most simple for the homonuclear dimer and $D_{\infty h}$ symmetry orbitals, generalizations to polyatomic systems can also be derived.

[23] These antibonding states are characterized by a general transfer of charge out of the bond region and consequentially less effective shielding of the nuclear charge. [See Figs. 6(b) and 7(b), Ref. 16.] However, the charge lobes in the bond region are localized close to the nuclei, and their attractive force on the reference nucleus can lead to a net attractive cohesive force (Table I).

[24] At this slightly compressed reference separation, there is a small net repulsive force of 0.07 hartree/bohr. This only differs from the value of Table III in rounding values for the tables.

[25] The same analysis for the minimum basis results of Table I gives a core orbital cohesive force of 10.21 eV/bohr which exceeds the valence orbital cohesive force of -9.90 eV/bohr to yield the net repulsion of 0.31 eV/bohr.

[26] The correct way to treat core electrons within a frozen core calculation, i.e., differentiation of the LSD functional *after* the frozen core approximation is introduced, has been described [see J. Harris, R. D. Jones, and J. E. Mueller, J. Chem. Phys. **75**, 3904 (1981)]. Basis-set corrections of the gradient approach are not brought in, but forces of acceptable accuracy are reported for light atom molecules.

[27] Pseudopotential force calculations avoid core polarization problems in much the same way as in Ref. 26. [See also J. L. Martins, J. Buttet, and R. Car, Phys. Rev. Lett. **53**, 665 (1984) and references therein for applications to clusters.]