Representations of molecular force fields. I. Ethane: *Ab initio* and model, harmonic and anharmonic

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The quadratic and selected cubic force constants for ethane have been computed, using single determinant molecular orbital wavefunctions at the 4-31G level, with a view to testing and extending model consistent force fields (CFF) for "molecular mechanics" calculations. Results agree semiquantitatively with experiment, but experimental force constants of sufficient reliability to provide a definitive comparison are not yet available. In a comparison with the most rational general CFF available, that of Ermer and Lifson, the most significant discrepancies found to occur are those for certain stretch–bend couplings *assumed* to be zero in the CFF but shown to be appreciable by quantum calculation. It is observed that these couplings, but not the stretch–stretch couplings, are well accounted for by a steric interaction model. The *ab initio* cubic constants examined display the same pattern of conformity with a steric model. Bend–bend–bend and bend–bend–stretch but not all stretch–stretch–stretch interactions agree with those of the steric model. The partial success of the steric model shows that it is possible to represent a large number of interaction constants, quadratic and higher order, by a small number of parameters in molecular mechanics. The failure of the steric model to account for predominantly stretching interactions confirms that "classical" nonbonded interactions as embodied in conventional Urey–Bradley fields are not the only major contributors to off-diagonal force constants. An alternative model, the anharmonic model of Warshel, as modified by Kirtman *et al.*, was found to account well for pure stretches but not for bends or stretch–bend interactions.

I. INTRODUCTION

The construction of model force fields for calculating molecular conformations, bond lengths and bond angles, stabilities, and more recently, frequencies of vibration and thermodynamic functions, has been developed into a powerful and valuable tool ("molecular mechanics") for the study of organic substances.[1] It has been argued that, in suitable cases, the method yields answers just as precise as and much more inexpensively than those deduced directly from experiment.[2] The trouble is that existing procedures, while serving as reasonably reliable interpolation schemes for a related series of compounds, are of uncertain validity in extrapolations to other types of compounds. Also, current model fields fail to reproduce precisely all observables even in the case of molecules included in the set from which the adjustable constants were derived. A worthwhile goal is to find whether it is possible to construct transferable representations of force fields with physical significance beyond that of a mathematical interpolation routine. A fundamental stumbling block to progess is the paucity of reliable information on force fields of polyatomic molecules. For example, all quadratic but not cubic constants are known for methane while, for ethane and more complex molecules, not even the complete set of quadratic constants is known accurately. Therefore, we are investigating on several levels some approaches to improved reliability.

One particularly promising approach, in view of the rapid advances in *ab initio* computations of molecular energies,[3] is a theoretical calculation of selected components of force fields. Since hydrocarbons are the simplest organic compounds of relevance in conformational analyses, it seemed essential to investigate the force field of ethane in detail. For a beginning, single determinant SCF computations offer a useful semiquantitative guide despite the well-known quantitative deficiencies.[4] In the absence of reliable experimental data about force field components that are customarily neglected according to empirical rules of thumb (or out of sheer ignorance of the truth) it seemed useful to have at least rough theoretical guidelines for these components. These could be used to augment existing, incomplete, experimental fields and to assess various empirical models in the literature.

A great number of *ab initio* studies of the barrier to rotation and the influence of internal rotation on the other internal coordinates have already been published. This work, for the most part, was not duplicated in the present study. Shortly after our study began we learned of the computation by Pulay and Meyer of the quadratic force constants in ethane.[5] Since our purposes involved the derivation of selected anharmonic as well as harmonic interaction constants, and since our basis set was different, it was necessary to repeat the computation of the quadratic field in deriving the higher order terms.

Almost all model force fields are built around a diagonal valence force field to which atom–atom repulsive energies are added in some form. The repulsive terms are invariably included for $1 \cdots 4$ and more remote interactions. One of the main themes of the present work is to investigate whether there is a theoretical justification for the simple pairwise additive atom–atom repulsion models. In particular it is worthwhile to find whether such steric terms are reasonable to include in the "Urey–Bradley-like" $1 \cdots 3$ (geminal) interactions which are customarily omitted from model force fields

in "molecular mechanics." The following sections analyze this problem in some detail.

II. METHODS

A. *Ab initio* computations

Calculations of force constants were derived, without taking advantage of Pulay's computationally efficient procedure,[6] by calculating molecular electronic energies as a function of deformations along various symmetry coordinates. Molecular energies, designated below as V, were computed using single determinant *ab initio* molecular orbital wavefunctions at the split valence shell, 4–31 G level.[3]

The force constants reported here are defined by the convention

$$V = \frac{1}{2}\sum_i\sum_j F_{ij}S_iS_j + \sum_{i\leq j\leq k}\sum\sum F_{ijk}S_iS_jS_k \ . \tag{1}$$

Since the equilibrium structure of ethane is not known with precision, the symmetry coordinates S_i were reckoned relative to the reference structure suggested by the *ab initio* calculations themselves. In deriving force constants the approximate equilibrium structure deduced previously was adopted for a reference structure, taking $r_{CH} = 1.083$ Å, $r_{CC} = 1.529$ Å, and angle HCH = 107.70°. The additional information derived in the present research later established a slightly more precise 4–31 G equilibrium structure: $r_{CH} = 1.08339$ Å, $r_{CC} = 1.52888$ Å, and angle HCH = 107.7258°. A representation of the molecular orbital energies by a Taylor series expansion about the original reference geometry included linear terms in A_{1g} coordinates to compensate for the fact that the reference geometry was not exactly that of the minimum energy coordinates. Schwendeman's recommendation[7] that theoretical force constants be calculated from the experimental rather than theoretical potential energy minimum is not seriously violated in any case, and the cubic constants reported in a later section make it possible to recalculate many of the quadratic constants for an arbitrary reference structure if desired. Schwendeman's argument concerns the dependence of the second derivatives of the potential energy upon the displacements of the atoms. For example, for a bond stretch, the Morse curve $\frac{1}{2}k(x^2 - ax^3 + \cdots)$, where $x = r - r_e$, possesses a second derivative $k(1 - 3ax + \cdots)$. Since a is in the vicinity of 2 Å^{-1} for many bonds, a spurious linear term shifting a potential minimum away from the equilibrium length r_e by 0.01 Å may alter a force constant by about 6%. Bending force constants are less sensitive to bond lengths and reference structures. In view of the level of *ab initio* theory brought to bear on the problem and the substantial uncertainty in experimental force constants, an uncertainty of several percent would seem to be tolerable for the present purposes. Even if the uncertainty were several-fold greater for the interaction constants, the results would still be more precise than those available from experiment.

Our C–H bond length is somewhat shorter than the *equilibrium* bond length in methane estimated empirically to be about 1.085 Å by Kuchitsu and Bartell[8] and com-

puted to be 1.091 Å by Meyer.[9] Electron diffraction studies[8,10] suggest that the bonds in methane may be about 0.003 Å shorter than in ethane, and 4–31 G calculations[3] make the difference 0.002 Å. The C–C reference length is between the electron diffraction r_g value[10] of 1.533 Å and the equilibrium length of approximately 1.526 Å estimated from r_g by invoking the correction $3al^2/2$.[11] Experimental HCH angles in ethane are 107.4° after Kuchitsu's vibrational corrections.[12]

Molecular deformations used in the force field determination ranged up to 0.056 Å for CH stretches, 0.04 Å for the CC stretch, and 7° for bends. Diagonal force constants F_{ii} and F_{iii} (and for A_{1g}, F_i) were initially derived by least squares analyses of the data for deformations along pure symmetry coordinates. The small effects of the A_{1g} quartic contributions were taken into account by giving the *ratio* F_{iiii}/F_{iii} its Morse curve value. Once the diagonal constants were established, the interaction constants were determined from energies for mixed deformations. Sets of matched pairs of molecular configurations were taken for which the sums (or differences) in energy would isolate certain interactions and cancel others. This procedure yielded the Taylor expansion coefficients F_{ij} and F_{iij} definitively. Differences between the original energies and those calculated from the Taylor expansion were, for the most part, of the order of the roundoff errors in the former values. A tabulation of configurations for which computations were run, together with the associated energies and residuals, is available from ASIS.[13]

The torsion–torsion–stretch force constant F_{443}, was evaluated indirectly from a calculation of δR, the difference between minimum energy C–C bond lengths for eclipsed and for staggered conformations when none of the other internal coordinates were allowed to relax. This difference was found to be 0.015 Å. We assumed that the C–C bond length varies with torsion angle τ as

$$R - R_e = (1 - \cos 3\tau)\delta R/2 \tag{2}$$

or, if τ is small,

$$R - R_e \approx 9\tau^2\delta R/4 \ . \tag{3}$$

The associated terms in potential energy are, if $S_3 \equiv R - R_e$ and $S_4 \equiv \tau$,

$$V(S_3, S_4) = \cdots + \frac{1}{2}F_{33}S_3^2 + F_{443}S_4^2S_3 + \cdots \ , \tag{4}$$

from which[14]

$$\partial V/\partial S_3 = F_{33}S_3 + F_{443}S_4^2$$
$$= 0 \text{ at minimum } V \ , \tag{5}$$

or

$$(S_3)_{min} = -F_{443}S_4^2/F_{33} \ . \tag{6}$$

Comparing Eqs. (3) and (6) we find

$$F_{443} = -9F_{33}\delta R/4 \ . \tag{7}$$

B. Steric model

Notwithstanding the abundant evidence supporting the existence of intramolecular repulsive interactions between atoms that are not covalently bonded to each

TABLE I. Parameters for Buckingham potential functions, $Ae^{-\alpha r} - Br^{-6}$, energy in mdyn Å, distance in Å.[a]

Interaction	A	α	B
H $\cdots$ H	14.72	3.4	0.3333
C $\cdots$ H	135.4	3.75	1.076

[a]C–H foreshortening, 0.117 Å.

other, the quantitative assessment of nonbonded interaction energies has eluded chemical physicists. The very good reason for this is the fact that, while almost everyone has an intuitive and doubtlessly qualitatively correct notion of what such interactions mean, no one has been able to define them rigorously and unambiguously. Molecular energies are measurable or calculable as a function of molecular geometry but their apportionment into interpretable components is arbitrary now and is likely to remain so, insofar as purely *ab initio* theory is concerned. Empirical recipes incorporating steric interactions are successful enough qualitatively, however, to justify a continued search for a satisfactory model.[1]

The model adopted here is not intended to represent a final optimization, for it is a far too simple, pairwise additive model known to be inexact in representing such an elementary system as $H_2 \cdots H_2$. Our model is a plausible compromise originally introduced to test an entirely different concept in organic conformational analysis. In its construction, described in detail elsewhere,[14] H $\cdots$ H interactions were inferred from a curve fit in the mean of Kochanski's *ab initio* calculations on $H_2 \cdots H_2$ interactions[15]; C $\cdots$ H and C $\cdots$ C interactions (the latter irrelevant for ethane) were derived to be compatible, on the one hand, with the force field of Schachtschneider and Snyder[16] and, on the other, with known structures and isomerization energies of hydrocarbon molecules. The virtue of the model is its ability to correlate a fairly wide range of observations simply and semiquantitatively. It is not unreasonable unless taken too literally. Beyond that no fundamental claims are made. Its essence is that nonbonded atoms interact, pairwise, according to Buckingham potential functions $(A e^{-\alpha r} - Br^{-6})$ in which the parameters A, α, and B are listed in Table I. The variable r is the distance between atomic interaction centers which, in the case of hydrogen (but not carbon) are "foreshortened" as suggested by Williams,[17] to be a distance Δ away from the proton toward the atom to which the proton is covalently bonded. From Kochanski's calculated energies[15] we have assigned to Δ the value of 0.117 Å.

The derivation of the steric components of F_{ij} and F_{iij} was done by setting

$$V = \sum V_{kl} + V_{\text{remainder}} ,$$

in which the Buckingham functions V_{kl} between atoms k and l are summed over all nonbonded distances or specified subsets of nonbonded distances. The steric components contributed by interaction kl to F_{ij} or F_{iij}, for example, are $(F_{ij})_{kl} = \partial^2 V_{kl}/\partial S_i \partial S_j$ or $(F_{iij})_{kl} = \frac{1}{2}(\partial^3 V_{kl}/$
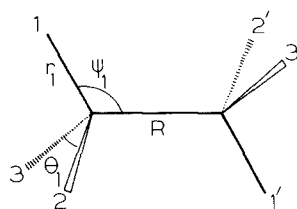

FIG. 1. Notation for internal coordinates of ethane.

$\partial S_i^2 \partial S_j)$. These quantities were evaluated by numerical differentiation and were checked analytically in some cases.

C. Coordinates and transformations

Internal coordinates, identified in Fig. 1, follow the notation of Hansen and Dennison.[18] Their relation to symmetry coordinates is given in Table II where the sign conventions follow Duncan[19] rather than Pulay and Meyer[5] and where the A_{1g} and A_{2u} bend coefficients are those appropriate for nontetrahedral angles. For the purposes of the present paper, we adopt the curvilinear symmetry coordinates for bends expressed literally in terms of the expressions in Table II instead of the more common linear combinations of Cartesian displacement coordinates. Our convention strongly influences the values of the cubic constants F_{ijk} but avoids mixing stretches into the bending coordinates.

As an aid in interpretation of results and to help facilitate comparisons with other published work, the quadratic force constants F_{ij} of Eq. (1) were transformed into those for a general valence force field

$$2V = \sum_i \sum_j k_{ij} R_i R_j . \tag{2}$$

TABLE II. Symmetry coordinates for ethane.[a]

A_{1g}:

$S_1 = 6^{-1/2} \sum_i (\Delta r_i + \Delta r_i')$

$S_2 = 12^{-1/2} [A \sum_i (\Delta\theta_i + \Delta\theta_i') - B \sum_i (\Delta\psi_i + \Delta\psi_i')]$

$S_3 = \Delta R_{cc}$

A_{1u}:

$S_4 = \tau$

A_{2u}:

$S_5 = 6^{-1/2} \sum_i (\Delta r_i - \Delta r_i')$

$S_6 = 12^{-1/2} [A \sum_i (\Delta\theta_i - \Delta\theta_i') - B \sum_i (\Delta\psi_i - \Delta\psi_i')]$

E_u:

$S_7 = 12^{-1/2} [(2\Delta r_1 - \Delta r_2 - \Delta r_3) - (2\Delta r_1' - \Delta r_2' - \Delta r_3')]$

$S_8 = 12^{-1/2} [(2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3) - (2\Delta\theta_1' - \Delta\theta_2' - \Delta\theta_3')]$

$S_9 = 12^{-1/2} [(2\Delta\psi_1 - \Delta\psi_2 - \Delta\psi_3) - (2\Delta\psi_1' - \Delta\psi_2' - \Delta\psi_3')]$

E_g:

$S_{10} = 12^{-1/2} [(2\Delta r_1 - \Delta r_2 - \Delta r_3) + (2\Delta r_1' - \Delta r_2' - \Delta r_3')]$

$S_{11} = 12^{-1/2} [(2\Delta\theta_1 - \Delta\theta_2 - \Delta\theta_3) + (2\Delta\theta_1' - \Delta\theta_2' - \Delta\theta_3')]$

$S_{12} = 12^{-1/2} [(2\Delta\psi_1 - \Delta\psi_2 - \Delta\psi_3) + (2\Delta\psi_1' - \Delta\psi_2' - \Delta\psi_3')]$

[a]$A = [2\gamma/(1+\gamma)]^{1/2}$, $B = [2/(1+\gamma)]^{1/2}$, $\gamma = 12\cos^2\psi_e/(4 - 3\sin^2\psi_e)$, $\psi_e = $ equilibrium < HCC. At $\psi_e = 109.4712°$, $\gamma = A = B = 1$.

TABLE III. Transformations of symmetry force constants to valence force constants. [a]

$$k_r = \frac{1}{6}(F_{11} + F_{55} + 2F_{77} + 2F_{10,10}).$$

$$k_R = F_{33}.$$

$$k_{rr} = \frac{1}{6}(F_{11} + F_{55} - F_{77} - F_{10,10}).$$

$$k_{rR} = 6^{-1/2} F_{13}.$$

$$k_{rr'} = \frac{1}{6}(F_{11} - F_{55} - 2F_{77} + 2F_{10,10}).$$

$$k_{rr'_\beta} = \frac{1}{6}(F_{11} - F_{55} + F_{77} - F_{10,10}).$$

$$k_{r\theta} - k_{r\theta\beta} = \frac{1}{2}(F_{78} + F_{10,11}).$$

$$k_{r\psi} - k_{r\psi\beta} = \frac{1}{2}(F_{79} + F_{10,12}).$$

$$Ak_{r\theta\beta} - Bk_{r\psi\beta} = \frac{1}{6}[2^{1/2}(F_{12} + F_{56}) - A(F_{78} + F_{10,11}) + B(F_{79} + F_{10,12})].$$

$$Ak_{R\theta} - Bk_{R\psi} = 3^{-1/2}F_{23}.$$

$$k_{r\theta'} - k_{r\theta'_\beta} = \frac{1}{2}(-F_{78} + F_{10,11}).$$

$$k_{r\psi'} - k_{r\psi'_\beta} = \frac{1}{2}(-F_{79} + F_{10,12}).$$

$$Ak_{r\theta'_\beta} - Bk_{r\psi'_\beta} = \frac{1}{6}[2^{1/2}(F_{12} - F_{56}) + A(F_{78} - F_{10,11}) - B(F_{79} - F_{10,12})].$$

$$k_\theta - k_{\theta\theta} = \frac{r^2}{2}(F_{88} + F_{11,11}).$$

$$k_\psi - k_{\psi\psi} = \frac{1}{2}(F_{99} + F_{12,12}).$$

$$k_{\theta\psi} - k_{\theta\psi\beta} = \frac{1}{2}(F_{89} + F_{11,12}).$$

$$A^2 k_{\theta\theta} + B^2 k_{\psi\psi} - AB(k_{\theta\psi} + k_{\theta\psi\beta}) = \frac{1}{6}[2(F_{22} + F_{66}) - A^2(F_{88} + F_{11,11})$$
$$- B^2(F_{99} + F_{12,12}) - AB(F_{89} + F_{11,12})].$$

$$k_{\theta\theta'} - k_{\theta\theta'_\beta} = \frac{1}{2}(-F_{88} + F_{11,11}).$$

$$k_{\psi\psi'} - k_{\psi\psi'_\beta} = \frac{1}{2}(-F_{99} + F_{12,12}).$$

$$k_{\theta\psi'} - k_{\theta\psi'_\beta} = \frac{1}{2}(-F_{89} + F_{11,12}).$$

$$A^2 k_{\theta\theta'_\beta} + B^2 k_{\psi\psi'_\beta} - AB(k_{\theta\psi'} + k_{\theta\psi'_\beta}) = \frac{1}{6}[2(F_{22} - F_{66}) + A^2(F_{88} - F_{11,11})$$
$$+ B^2(F_{99} - F_{12,12}) + AB(F_{89} - F_{11,12})].$$

[a] $A = [2\gamma/(1+\gamma)]^{1/2}$, $B = [2/(1+\gamma)]^{1/2}$, $\gamma = 12 \cos^2\psi_e/(4 - 3\sin^2\psi_e)$.

The convenient notation of Hansen and Dennison[18] to indicate various interactions was adopted to identify the *pairs of coordinates involved* but the *magnitudes* of the k_{ij} correspond to Eq. (2) and *not* to the different conven-

TABLE IV. *Ab initio* symmetry force constant matrices for ethane with estimated errors owing to roundoff. [a] Energy in mdyn Å.

		This work[b]			Pulay and Meyer[c]		
A_{1g}							
	5.861 (4)	0.150 (4)	0.204 (6)	5.685	0.099	0.198	
		0.754 (1)	−0.581 (1)		0.789	−0.551	
			4.877 (50)			5.073	
A_{2u}	5.868 (6)	0.186 (1)		5.671	0.147		
		0.689 (1)			0.723		
E_u	5.762 (6)	−0.195 (1)	0.093 (1)	5.578	−0.211	0.128	
		0.687 (6)	0.018 (8)		0.693	−0.012	
			0.605 (12)			0.657	
E_g	5.675 (6)	−0.199 (40)	0.196 (40)	5.508	−0.229	0.284	
		0.724 (3)	−0.029 (20)		0.683	−0.004	
			1.001 (12)			1.043	

A_{1g} linear coefficients

$F_1 = -0.0057$ (3) $F_2 = -0.0014$ (1) $F_3 = 0.0013$ (4)

[a] Last figure in parentheses corresponds to last decimal in listed value.
[b] $E_{min} = -79.115\,931$ a. u. .
[c] Reference 5, $E_{min} = -79.105\,436$ a. u. .

tions of Hansen and Dennison. Interactions are identified in Fig. 2. Relations governing the transformations of the F_{ij} into the k_{ij} are given in Table III for the most general expression consistent with Eqs. (1) and (2).[20] Not all k_{ij} are observable of course, but the tabulated combinations are, in principle. Steric components of the magnitudes of the k_{ij} were derived from Shimanouchi's Urey–Bradley equations[21] by identifying the U. B. F'_{kl} and F_{kl} with $r_{kl} V'_{kl}$ and V''_{kl}, respectively.

III. RESULTS

Ab initio symmetry force constants F_{ij} are listed in Table IV together with the A_{1g} linear expansion coefficients F_i. Crude estimated probable errors of no statistical validity were calculated assuming residuals were random. They are listed in parentheses as a rough
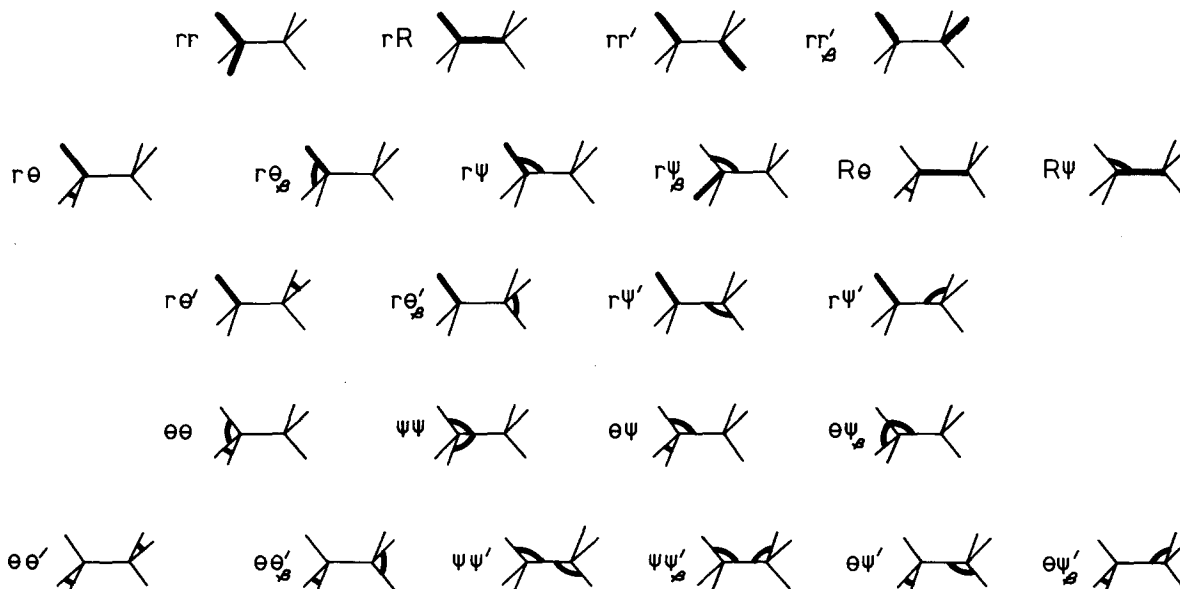

FIG. 2. Notation for interaction constants in ethane.

TABLE V. General valence force constants for C_2H_6, energy in mdyn Å.

Constant	Calculated			Experimental	
	ab initio MO[a]	CFF model[b]	Steric model[c]	H&D[d]	JLD[e]
k_r	5.767	4.735	⋯	5.35	4.810
k_R	4.877	4.483	⋯	4.57	4.450
k_{rr}	0.049	0	0.327	−0.02	0.045
k_{rR}	0.083	0	0.447	0.0	(0)
$k_{rr'}$	−0.030	0	0	0.08	−0.036
$k_{rr'\beta}$	0.013	0	0	−0.04	0.015
$k_{r\theta} - k_{r\theta\beta}$	−0.197	0	−0.161	−0.11	−0.076
$k_{r\psi} - k_{r\psi\beta}$	0.145	0	0.234	−0.04	(0.076)[f]
$Ak_{r\theta\beta} - Bk_{r\psi\beta}$	0.194	0	0.165	−0.52	0.074
$Ak_{R\theta} - Bk_{R\psi}$	−0.335	−0.267	−0.359	−0.33	−0.282
$k_{r\theta'} - k_{r\theta'\beta}$	−0.002	≈0	0	−0.02	(0)
$k_{r\psi'} - k_{r\psi'\beta}$	0.052	≈0	0	−0.17	(0)
$Ak_{r\theta'\beta} - Bk_{r\psi'\beta}$	0.009	≈0	0	−0.10	(0)
$k_\theta - k_{\theta\beta}$	0.706	0.549	⋯	0.62	0.560
$k_\psi - k_{\psi\psi}$	0.803	0.672	⋯	0.75	0.682
$k_{\theta\psi} - k_{\theta\psi\beta}$	−0.006	0	0	−0.04	0.008
$[A^2 k_{\theta\theta} + B^2 k_{\psi\psi} - AB(k_{\theta\psi} + k_{\theta\psi\beta})]$	−0.018	−0.055	0	0.06	−0.012
$k_{\theta\theta'} - k_{\theta\theta'\beta}$	0.019	≈0	0	−0.02	−0.006
$k_{\psi\psi'} - k_{\psi\psi'\beta}$	0.198	0.104	0	0.13	0.139
$k_{\theta\psi'} - k_{\theta\psi'\beta}$	−0.024	≈0	0	0.09	0.005
$[A^2 k_{\theta\theta'\beta} + B^2 k_{\psi\psi'\beta} - AB(k_{\theta\psi'} + k_{\theta\psi'\beta})]$	−0.039	−0.035	0	−0.09	−0.024

[a]This work.
[b]Reference 22.
[c]Based solely on geminal interactions.
[d]Reference 18.
[e]Reference 19.
[f]Constrained to be the negative of the previous value.

indication of the sensitivity of the derived parameters to numerical uncertainties. The *ab initio* quadratic force constants of Pulay and Meyer[5] are also listed, for comparison.

In Table V the general valence force field quadratic force constants calculated from the present *ab initio* calculations are compared with the experimental constants of Hansen and Dennison[18] and Duncan.[19] Also included are the model "consistent force field" constants proposed by Ermer and Lifson[22] and the coupling constants derived from the geminal steric model.

Listed in Table VI are selected cubic and quartic constants derived from the present MO calculations and from the geminal steric model. Estimated standard deviations in parentheses have the same meaning as they do in Table IV.

IV. DISCUSSION

A. Quadratic force constants

The reliability of the *ab initio* quadratic force constants listed in Tables IV and V cannot be assessed very rigor-

ously at present because no adequate reference values exist. It is known that force constants accurate to a few percent or a few hundredths of a mdyn/Å or mdyn Å/rad² were computed using comparable basis sets in the case of methane,[23] even for interaction constants, except for the stretch–stretch interaction which was systematically lower than the experimental value.[24] Differences between the results of Pulay and Meyer and ourselves are minor and owing, among other things, to the difference between the basis sets adopted, to the slightly different reference structures, and to the fact that the deformations from which Pulay and Meyer derived quadratic constants were comparable to those from which we derived cubic constants. Of somewhat greater interest to chemists because of their more widespread use in transferable representations of force fields are the general valence force constants; these are listed in Table V for ethane. The agreement of the *ab initio* results with experiment is encouraging but not entirely definitive. Our diagonal force constants are in better agreement with those of Hansen and Dennison[18]

TABLE VI. Selected anharmonic force constants for ethane with estimated errors owing to roundoff. Energy in mdyn Å.

Force constant	*ab initio* MO	Geminal steric model	Kirtman– Warshel model
Diagonal stretch			
F_{111}	−2.086 (10)	⋯	−2.033
F_{333}	−3.909 (2)	⋯	−3.333
$F_{10,10,10}$	−1.513 (30)	⋯	⋯
Diagonal bend			
F_{222}	0.081 (2)	0.050 CH, HH (0.069)[a]	−0.021
$F_{11,11,11}$	−0.007 (5)	−0.014 HH	⋯
$F_{12,12,12}$	−0.071 (20)	−0.070 CH	⋯
Coupling F_{iij}			
i = stretch, *j* = 3			
F_{113}	0.1446 (3)	−0.578 CH	0
F_{553}	0.144 (30)	−0.578 CH	0
F_{773}	0.132 (30)	−0.578 CH	0
$F_{10,10,3}$	0.160 (30)	−0.578 CH	0
i = bend, *j* = 3			
F_{223}	−0.262 (1)	−0.335 CH	−0.003
F_{663}	−0.172 (6)	−0.335 CH	−0.003
F_{883}	0.014 (30)	0	0
F_{993}	−0.466 (6)	−0.611 CH	−0.006
$F_{11,11,3}$	0.043 (30)	0	0
$F_{12,12,3}$	−0.456 (6)	−0.611 CH	−0.006
i = torsion, *j* = 3			
F_{443}	−0.165 (5)	0	
i = bend, *j* = 2			
F_{222}	0.081 (2)	0.050 CH, HH	−0.021
F_{266}	0.282 (50)	0.149 CH, HH	−0.064
F_{288}	−0.173 (10)	−0.218 HH	−0.254
F_{299}	0.089 (20)	0.174 CH	0.154
$F_{2,11,11}$	−0.175 (10)	−0.218 HH	−0.254
$F_{2,12,12}$	0.132 (18)	0.174 CH	0.159
Miscellaneous			
F_{122}	⋯	−0.14	−0.001
F_{133}	−1.48 (15)	−1.92	0
$F_{1,11,11}$	⋯	−0.10	−0.000
F_{233}	0.45 (2)	0.94	0.082
F_{1133}	10.9 (30)	2.3	⋯
F_{8888}	0.4 (3)	⋯	⋯
F_{9999}	0.83 (15)	⋯	⋯

[a]This constant also includes vicinal *gauche* H⋯H interactions.

than with those of Duncan,[19] presumably because Hansen and Dennison made approximate corrections of frequencies to remove anharmonic effects while Duncan did not. On the other hand, the least-squares solutions of Hansen and Dennison, with few constraints, were somewhat ill conditioned with the result that the interaction constants seem to contain a certain amount of scatter. Duncan's solutions were well conditioned because of the constraints imposed (see parentheses) but the zero values assumed for some constants and the contamination by anharmonicity influence the values derived for most constants.

In view of our aim of obtaining more information for theoretical conformational analysis, it is of special interest to compare the ab initio constants with those of proposed model fields. Many of the latter exist, some of which, representing somewhat arbitrary adjustments to account for a limited range of data not including vibrational spectra, are not appropriate to list here. One of the more promising approaches in theoretical conformational analysis is the development by Lifson and Warshel of so-called "consistent force fields" (CFF) which, with one standard formula, are supposed to reproduce vibrational spectra, thermodynamic data, and molecular structures.[22,25] This formula, in its various versions, may contain some two dozen parameters including potential constants and reference bond lengths and angles. These parameters are adjusted systematically by least-squares comparisons with experimental data. Since even ethane, simple though it be, contains 22 independent quadratic force constants, not to mention higher order terms and structure parameters, it is clear that the CFF formulas to date, while very useful representations, must be simplified compromises. One of the most recent CFF, developed by Ermer and Lifson,[22] is listed in Table V as it applies to ethane. Certain tabulated force constants identifiable by ≈ 0 do not include the effect of remote H $\cdots$ H interactions which, according to the CFF formula, are nonvanishing but small. The CFF constants were adjusted, as were Duncan's, to fit observed frequencies rather than frequencies corrected for anharmonicity.

For comparison purposes are listed the coupling constants calculated from the naive steric model (Sec. II. B) including only geminal (1 $\cdots$ 3) interactions. It is noteworthy that the major discrepancies between the ab initio and model CFF force field are roughly accounted for by the steric interaction model.[26] It must be emphasized that the steric model was in no way adjusted to account for the ethane calculations; it was proposed prior to the completion of the ab initio computations. The steric interactions are at their best in representing bend–stretch interactions and, as discussed below, bend–bend–stretch cubic terms. Plotted in Fig. 3 is a comparison of ab initio and steric interaction constants involving bending modes. A strong correlation is revealed even though the agreement is not quantitative. Model steric interactions are much less successful in mimicking the ab initio results in the case of stretch–stretch constants. This may be, in part, attributable to the fact noted earlier in a discussion of methane calculations that Hartree–Fock computations tend to under-

value stretch–stretch couplings. More important, however, is an interaction compensating for the steric contribution to stretch–stretch constants between C–H bonds. In an early discussion of this compensating interaction (designated as $G \Delta r_i \Delta r_j$)[27] evidence was adduced suggesting that compensation is due in part to the influence of protons in altering the effective atomic numbers of the atoms to which they are bonded. Urey–Bradley analyses[28] had long indicated that halogen-halogen intramolecular repulsions seem to follow "normal" classical nonbonded force laws while H $\cdots$ H geminal interactions seem anomalously low—much lower than calculated by Mulliken,[29] for example. Such an anomaly can be accounted for by significant interaction constants for protons of the above form with $G < 0$, but whether the "G" is best accounted for by orbital exponent changes or, say, by "unbalanced coupling" of nonbonded hydrogen orbitals as discussed later, is not settled. In either case, the interaction masking steric contributions to stretch–stretch couplings would be expected to be less effective in obscuring steric coupling arising from bending displacements.

B. Cubic force constants

Of the great number of possible cubic force constants in ethane, we shall focus attention upon two kinds, certain diagonal constants F_{iii} and the F_{iij} with j an A_{1g} coordinate. The F_{iii} are nonvanishing, of course, only for g symmetry coordinates. It was of interest to examine the C–H and C–C anharmonic terms for stretching to see whether bonds in complex polyatomic molecules conform to the Morse-like pattern characterizing diatomic and at least some triatomic molecules. As mentioned in a previous section, a Morse curve can be written as $(k/2)(x^2 - ax^3 + \cdots)$ where a is commonly of the order of 2 Å^{-1}. The F_{111} and F_{333} values in Table VI
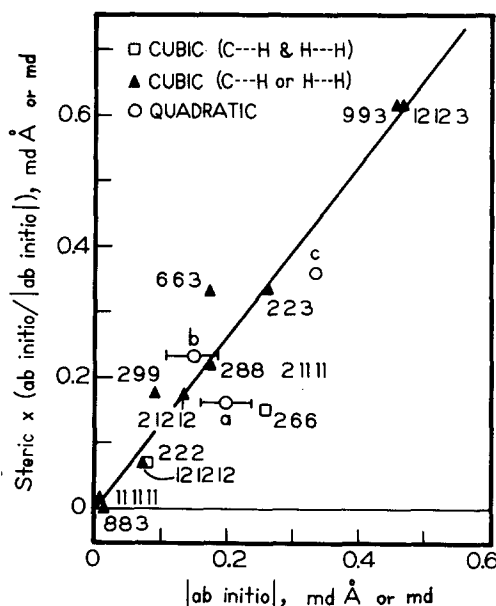

FIG. 3. Quadratic and cubic force constants for ethane as calculated from ab initio molecular orbital energies and from steric model. Cubic constants are identified in the figure. Quadratic constants correspond to (a) $(k_{r\theta} - k_{r\theta\theta})$, (b) $(k_{r\phi} - k_{r\theta\theta})$, and (c) $(k_{R\theta} - k_{R\phi})$.

are consistent with a values of 1.8 Å^{-1} and 1.7 Å^{-1}, respectively. Because of the incorrect dissociation products corresponding to SCF wavefunctions,[4] there is a widespread belief that quadratic constants tend to be high and cubic constants, low, which would make a too low. Meyer and Pulay[23] have noted that SCF wavefunctions may yield better force fields than commonly thought. In our calculations, the a values are roughly those expected for Morse-like bonds though, in the case of F_{111}, a is a little lower than estimated in some previous work.[8]

Of perhaps greater interest because of the lack of established rules of thumb is the magnitude of the constant F_{222} for pure bending. Kuchitsu and Morino[30] have reported evidence that bending anharmonicity is small. For example, while r_e and the vibrational mean, r_z, are substantially different from each other for bond lengths, for bond angles α_e and $\langle\alpha\rangle$ are usually taken to be almost identical. Our computed $F_{222} = 0.081$ mdyn Å/rad^3 is small and of the magnitude given by the steric model, as seen in Table VI. In the case of F_{222} we calculated the vicinal H $\cdots$ H (*gauche*) as well as the geminal H $\cdots$ H and geminal C $\cdots$ H model contributions and found them to be 0.019, -0.014, and 0.064 mdyn Å/rad^3, respectively. Vicinal steric interactions should be smaller for the other constants listed.

A justification for studying the F_{ii1}, F_{ii2}, and F_{ii3} interactions is that it is these which can give rise to a secondary isotope effect in the structure of ethane. That is, as was predicted on the basis of a crude steric model many years ago,[31] the mean $\langle r_z \rangle$ C–C bond length should be different in C_2H_6 and C_2D_6. Such isotope effects are almost universally neglected in reducing experimental rotational constants to experimental molecular structures even though Kuchitsu has shown that this neglect may lead to appreciable errors.[12] It is important, then, to establish the possible magnitude of the constants coupling bond lengths to amplitudes of vibration of adjacent bonds. A treatment of the constants listed in Table VI confirms that secondary isotope effects of the order of magnitude originally guessed from steric considerations[31] can arise. This treatment is published elsewhere.[32]

Since the motivation for the present work was to provide information and insights for modeling molecular force fields, it is of interest to include for comparison the results of a model anharmonic "consistent force field" for ethane proposed by Warshel[33] and modified by Kirtman, Palke, and Ewig.[34] Warshel used empirical information to determine Morse-type stretching and angular potential parameters. Kirtman *et al.* resolved certain parameters in the cubic part of the pure angular potential with the aid of *ab initio* computations. Results which can be compared with the present computations are listed in Table VI. The Kirtman modification evidently works well for pure stretching deformations but is less successful in representing bends and C–H, C–C interactions.

[*Note added in proof*. We have now examined the geminal nonbonded interactions that are included in Warshel's original paper[33] but deleted in the treatment by Kirtman *et al.*[34] These nonbonded energies themselves are very different from those of the present paper, and the third derivatives of H $\cdots$ H are much lower, as well. The C $\cdots$ H third derivatives are quite similar to our own, however and, accordingly, those cubic constants in Table VI depending largely on C $\cdots$ H interactions (see middle column) would turn out in the Warshel model to be similar to those of our geminal steric model.]

The steric model (Sec. II.B and Table I) yields values for the stretch–stretch–stretch constants F_{ii3} that are not only wrong in magnitude but in sign. This failure of a model including only purely space-filling atom–atom interactions is not particularly surprising when considered from the viewpoint of the next section. What is more surprising and of potential utility in constructing model fields for molecular mechanics is the fairly good agreement of the F_{iij} where i is a bend (see Fig. 3).

One significant feature of the *ab initio* cubic constants F_{ii3} for pure stretches is that, even though they are in considerable disagreement with the steric model, they show the same lack of dependence upon i. This is consistent with a model of interactions between the C–H bonds and the C–C bond in which the various C–H bonds act nearly independently of each other. A similar approximate independence in the bend–bend–stretch F_{ii3} and in the F_{ii2} exists as evinced by the parallel behavior between the *ab initio* and steric results. Here, normalization artifacts (rather than bond cooperative effects) destroy the constancy of the F_{ii3} for $i = 2$, 6, 9, and 12.

The most noteworthy conclusion derivable from the cubic interaction constants is that they follow the same pattern as do the quadratic interactions. That is, they are in accord with a steric coupling picture when bending modes are involved but not when all the modes are pure stretches. This result parallels the findings of Kuchitsu and Morino for triatomic molecules. Kuchitsu and Morino observed that the experimental cubic constants $k_{\alpha\alpha\alpha}$ and $k_{r\alpha\alpha}$ are more or less in conformity with a model of nonbonded repulsions[30] but that $k_{rr\alpha}$ is less well represented by such a model. That the pure stretch constant F_{133} is in much better agreement with a steric model than is F_{113} is consistent with the special role of protons proposed in Ref. 27 and mentioned in Sec. A above.

It is instructive to make a further observation about the cubic constants in the class most likely to correlate with a *geminal* steric model, namely the class including at least two bending coordinates. Of these, all but F_{222} and F_{266} depend solely upon one type of interaction, either C $\cdots$ H or H $\cdots$ H, as designated in Table VI. Constants F_{222} and F_{266} (which equals $3F_{222}$ identically in the geminal steric model) involve the *difference* between interactions, C $\cdots$ H tending to make F_{222} positive, and H $\cdots$ H tending to make it negative. It is interesting that F_{222} and F_{266} are the constants conforming most poorly with the geminal steric model, perhaps because they are the only constants depending upon a delicate balance between two different interactions. Presumably a steric model could be optimized to be in

much better accord with the molecular interactions than is our model (Table I) which was formulated prior to the calculations of *ab initio* cubic constants.

C. Further comments on steric model

Mulliken's treatment[29] of H $\cdots$ H nonbonded interactions in hydrides such as methane gives $V(r_{HH})$ values closely resembling those inferred from the *ab initio* calculations[15] for the system $H_2 \cdots H_2$ and, hence, closely resembling those of the present steric treatment. Mulliken's treatment is a variant of the EHMO method popularized later by Hoffmann.[35] Now, it is possible to express EHMO energies as a sum $\sum E_{ij}$ over all atoms i and j in a molecule. It has been found that the EHMO method yields surprisingly good bending force constants and fair interaction constants for hydrocarbons such as methane, ethane, and ethylene,[36] but that the E_{ij} for nonbonded atoms do not resemble the $V(r_{ij})$ of Mulliken's approach unless atoms i and j are in different molecules or are separated by a large number of covalent bonds. The nonbonded E_{ij} for hydrogens in ethane account for a major amount of the barrier to rotation in ethane in an interpretation made quite persuasively by Lowe.[37] The Mulliken method, exploited fruitfully by Müller,[38] corresponds to assuming that the overlap populations for pairs of nonbonded orbitals simulate those for pairs of rare gas atoms to the extent that they represent a balanced population of bonding and antibonding molecular orbitals. This balance extinguishes the strong (covalent) E_{ij} terms linear in overlap integrals and leaves a second-order residual corresponding closely to the conventional concept of "classical nonbonded interactions." On the other hand, it turns out in practice that interactions between nonbonded orbitals separated by only a few bond lines are overbalanced by phase relations that favor making the intervening covalent bonds strong, often at the expense of making the less important "nonbonded interactions" considerably more destabilizing than they would be according to the "balanced coupling" implicit in Mulliken's approach. Thus, *gauche* H $\cdots$ H interactions in ethane suffer an appreciable excess of covalent antibonding in order to make CH and CC bonds strong, whereas *anti* H $\cdots$ H interactions, aimed favorably, are especially stabilizing. Lowe,[37] and Hoffman *et al.*,[39] among others,[40] have described useful diagrammatic representations of certain hyperconjugative and other interactions modulating "nonbonded interactions."

The point of this qualitative discussion of nonbonded interactions is to indicate that there are good reasons for expecting a simple steric model to be inadequate in treating nonbonded interactions if the atoms are separated by a chain of only a few covalent links. Yet, if we let the lion's share of the change in interactions during torsional displacements be represented by an "intrinsic" barrier function to account for the unbalanced couplings and superpose on this some simple steric components, we get a fair representation of trends in hydrocarbon barriers.[41] Moreover, experimental Urey–Bradley analyses by Shimanouchi[28] and others[27] present provocative evidence favoring simple steric origins of intramolecular interactions. Finally, the present work

itself provides considerable support for the idea that, where bending modes are involved, a steric model yields semiquantitative results for interaction constants, cubic as well as quadratic. It may turn out that future formulations of force fields for more complex molecules than ethane can profitably take advantage of this clue about intramolecular forces.

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