Advanced Review

Anharmonic molecular force fields

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An anharmonic force field is defined as a higher-order Taylor-series expansion of the molecular potential energy surface (PES) around a reference geometry, usually chosen to be an equilibrium structure. Force field expansions provide excellent local approximations to PESs, one of the most important theoretical constructs of chemistry. This review deals principally with the definition and physical interpretation of anharmonic molecular force fields, their determination via techniques of electronic structure theory, their transformation among different rectilinear and curvilinear representations, and their utilization. Physical and technical factors leading to more precise and more accurate force fields are also discussed.

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INTRODUCTION

The concept of potential energy (hyper)surfaces (PESs) is fundamental to the understanding of most branches of chemistry. Mass-independent PESs are defined within the Born–Oppenheimer (BO) separation of the motions of the 'light' electrons and the 'heavy' nuclei.[1,2] PESs describe the variation of the total energy of a chemical system as a function of the position coordinates of the constituent nuclei. Adiabatic corrections to the BO-PES relax the strict separation, defining what one might call an adiabatic[3] PES, which is mass dependent.

In theoretical investigations of larger systems, increase in the dimensionality of the nuclear motion problem (there are 3*N*–3 degrees of freedom for an *N*-atomic molecule) precludes (nearly) complete treatments such as variational computation of rotational–vibrational energy levels. The complete characterization of the *global*, multidimensional PES of polyatomic molecules, depending on all the vibrational degrees of freedom, proves to be extremely challenging.[4–8] Therefore, simplifications must be introduced. Fortunately, in many areas of physical chemistry, the nuclear motion can be considered to be restricted to the vicinity of a single minimum. In this region, local characterization of the PES is often adequate. The most viable approach to the description of local PESs of larger polyatomic molecular systems involves the evaluation of anharmonic (usually quartic) force fields, defined as elements of a Taylor-series expansion of the PES around a reference geometry,[9–14] usually taken as the equilibrium position. Local PES representations should not be employed for molecular motions for which the harmonic oscillator model of vibrations cannot be considered as a good zeroth-order approximation, such as internal rotations/torsions with low barriers, pseudorotations, ring puckerings, and other cases of large-amplitude motions (LAM). Even for systems which exhibit LAM, the determination of anharmonic force fields about salient points on the PES can be used to solve the complementary-mode-coupling problem in the isolation of the floppy vibrations of concern in a vibrationally averaged Hamiltonian of reduced dimensionality. Overall, in many cases, an anharmonic force field representation of the PES should provide at least the first important stepping stone to understand the complex internal dynamics of the system.

Apart from the usual difficulties associated with 'inverse problems',[15] a major hindrance to the experimental determination of anharmonic force fields is the burgeoning number of force constants at higher orders as compared with the information content of the accessible data. As a consequence, reliable *experimental* anharmonic force fields are available for only a small number of exceedingly simple molecules. It cannot be hoped that experiments will provide complete anharmonic force fields even in the future. Determination of force fields via electronic structure computations is thus the only way forward. *Ab initio* electronic structure computations can yield high-quality global

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TABLE 1 | Names, Symbols, and Units for Vibrational Coordinates and Force Constants

Name	Symbol	SI Unit	Customary Unit
Vibrational coordinates			
Cartesian	X	m	Å
Internal			
Bond stretching	R_i, r_i	m	Å
Angle bending	α_i, Θ_i	radian	radian
Linear angle bending	λ_i	radian	radian
Out-of-plane bending	γ_i	radian	radian
Torsion	τ_i	radian	radian
Symmetry	S_i	(varies)	(varies)
Normal			
Mass adjusted	Q_r	kg$^{1/2}$ m	u$^{1/2}$ Å
Dimensionless	q_r	1	1
Vibrational force constants			
In internal coordinates	$f^{ijk\ldots}$	(varies)	(varies)
In symmetry coordinates	$F^{ijk\ldots}$	(varies)	(varies)
In dimensionless normal coordinates	$\phi^{rst\ldots}$	m^{-1}	cm^{-1}

and semiglobal PESs,[5,8,16–20] here determination of the functional form underlying the PES fitting is one of the largest obstacles. In the local, force field representation of the PES, this difficulty does not arise, anharmonic force fields can be computed and transformed straightforwardly. Complete anharmonic force fields have been determined for a large number of species. Molecules for which complete, at least quartic force fields have been obtained *ab initio* prior to 1998 are given in Table 1 of Ref 13. A few further representative examples of force field determinations are given in Refs 21–47. This list is highly incomplete, omission of articles is by no means intentional. Complete quartic force fields have been determined by wavefunction methods for molecules as large as the free amino acids glycine[42] and proline[40] (in the latter case, the force field for the 17-atom molecule with no symmetry contains 62,835 unique elements in the internal coordinate space).

Because of severe space limitations, the current review cannot be comprehensive in covering all relevant aspects of anharmonic force field determinations, not even those related to electronic structure computations, and it generally focuses on work from our group. Thus, probably several significant papers well worth reading are left out. In what follows, an attempt is made to cover, however briefly, the most important methodological aspects of computing anharmonic force fields.

THEORETICAL BACKGROUND

Molecular force fields are dependent upon the coordinate system and the reference structure chosen. The former determines the number of unique force constants, whereas both the former and the latter affect the accuracy of the force field determined and how the computed force field can be transformed from one coordinate representation to another. Given that an appropriate basis set and level of electronic structure theory are chosen, the necessary computations can be performed after one has considered how to obtain the high-order force constants from low-order analytic information without (much) loss of precision.

Definition and Interpretation of Force Constants

Expansion of the PES around a reference configuration is written in the following form:

$$
\begin{aligned}
V = V_0 &+ \sum_i f^i \mathbf{R}_i + \frac{1}{2}\sum_{ij} f^{ij} \mathbf{R}_i \mathbf{R}_j \\
&+ \frac{1}{6}\sum_{ijk} f^{ijk} \mathbf{R}_i \mathbf{R}_j \mathbf{R}_k + \frac{1}{24}\sum_{ijkl} f^{ijkl} \mathbf{R}_i \mathbf{R}_j \mathbf{R}_k \mathbf{R}_l \\
&+ \frac{1}{120}\sum_{ijklm} f^{ijklm} \mathbf{R}_i \mathbf{R}_j \mathbf{R}_k \mathbf{R}_l \mathbf{R}_m \\
&+ \frac{1}{720}\sum_{ijklmn} f^{ijklmn} \mathbf{R}_i \mathbf{R}_j \mathbf{R}_k \mathbf{R}_l \mathbf{R}_m \mathbf{R}_n + \ldots,
\end{aligned}
\tag{1}
$$

where $\mathbf{R}$ denotes an arbitrary set of *complete* and *nonredundant* nuclear displacement coordinates. If the expansion is set about a stationary point (e.g., an equilibrium geometry as usual), the gradient term in Eq. (1) disappears. In theoretical approaches, the force constants are evaluated directly; thus, introduction of redundant coordinates is usually an unnecessary complication, which should be avoided. Although in principle all complete and nonredundant coordinate sets are equivalent, some may have more desirable properties for certain applications than others. The factor ($1/n!$) in front of the nth-order sum in Eq. (1) ensures that the force constants are equal to the true derivatives of the potential energy V with respect to $\boldsymbol{R} = \{\boldsymbol{R}_i\}_{i=1}^{3N-6}$ taken at the reference configuration:

$$f^{ijk\ldots} = \frac{\partial^n V}{\partial \boldsymbol{R}_i \partial \boldsymbol{R}_j \partial \boldsymbol{R}_k \ldots} \qquad (2)$$

where the so-called quadratic, cubic, quartic, quintic, and sextic force constants will have 2, 3, 4, 5, or 6 superscripts, respectively. It is rare that complete force fields are determined up to sixth order,[26,27,31] usually only quartic force fields are obtained. Some authors prefer to use restricted summation in Eq. (1). The general relationship between force constants $f^{ijk\ldots}_{\text{restricted}}$ and $f^{ijk\ldots}$ is $f^{ijk\ldots}_{\text{restricted}} = f^{ijk\ldots} \prod a_r!$, where a_r is the number of equal indices of the rth type in the force constant in question. An $f^{ijk\ldots}$ is generally not well defined unless all the displacement coordinates, including those not explicitly involved in $f^{ijk\ldots}$, are specified.

The kinetic energy of a molecule is most easily expressed in (mass weighted, rectilinear) Cartesian coordinates. The potential energy has its most clear physical interpretation in (curvilinear) internal coordinates. When force constants are used to evaluate spectroscopic constants via second-order vibrational perturbation theory (VPT2),[23,25,48–50] (dimensionless) normal coordinates are employed. Thus, there are three important coordinate classes for the description of distortions from a reference structure: Cartesian, internal, and normal displacement coordinates. The recommended and customary usage of symbols and units for these coordinates and the related force constants are summarized in Table 1. Most researchers avoid the use of SI units, and define energies in aJ, and bond stretching and angle bending internal or symmetry coordinates in Å and radians, respectively. Therefore, the related force constants become, at nth order, aJ Å^{-n} for stretching and aJ rad^{-n} for bending coordinates. Units of interaction force constants follow these definitions.[51]

Force fields in Cartesian coordinates have no useful physical meaning. Higher-order normal coordinate force constants are also hard to interpret. However, force constants in most applied internal coordinate systems do have a clear physical interpretation.

Higher-order, *diagonal stretching* force constants almost always follow the patterns of relative signs and magnitudes of diatomic Morse oscillators[52,53]

$$V_{\text{M}}(r) = D_{\text{e}}[1 - \exp(-a\Delta r)]^2, \qquad (3)$$

where Δr is the displacement from equilibrium in the bond stretching coordinate, D_{e} is the dissociation energy from equilibrium, and a determines the harmonic force constant around equilibrium. The nth-order derivative of V_{M} around equilibrium is given as

$$f_{\text{M}}^{(n)} \equiv \frac{\partial^n V_{\text{M}}}{\partial r^n} = 2(-1)^n(2^{n-1} - 1)a^n D_{\text{e}}. \qquad (4)$$

Thus, simple relations connect the higher-order constants to lower-order ones, for example, $f_{\text{M}}^{(3)} = -3a f_{\text{M}}^{(2)}$ and $f_{\text{M}}^{(4)} = 7a^2 f_{\text{M}}^{(2)}$. As a is around 2 Å^{-1} for a large number of diatomics,[54] these relations allow semiquantitative estimates of higher-order stretching force constants. Note that the simple $1/r$ function as well as the Fues potential,[55] $\text{V}(r) = a_0 + a_1/r + a_2/r^2$, also yield the signs and magnitudes of higher-order stretching force constants.

Simple, chemically intuitive arguments would suggest that a quadratic, vicinal *stretch–stretch coupling* constant is positive: only in this case would elongation of one of the bonds lead to a decrease of the other. Indeed, most such force constants are positive. A simple counterexample is the case of the water molecule, where the $f^{rr'}$ coupling constant has a value of −0.1 aJ Å^{-2}. Another notable exception is f^{rR} of HCN,[25] where r and R represent the CH and CN stretches, respectively. Stretching a bond to the extreme results in a fragmentation of HCN into a diatom and an atom, and of the two possible products, H + CN is the more stable. The bond length of $X\,^2\Sigma^+$ CN is 1.172 Å, actually longer than that of HCN, that is, 1.153 Å. Thus, the negative sign of f^{rR} of HCN is explained.

A simple way to rationalize *quadratic stretch–bend* interactions in molecular force fields is provided, for example, by the hybrid orbital force field model of Mills.[56] The *stretch–bend interaction* constants of polyatomics can be either positive or negative and are often quite large, suggesting that the effective bending motion does not occur along a circular arc, corresponding to no change in the associated bond length. A possible way to visualize *higher-order off-diagonal* force constants is through derivative relations such as $f^{\lambda\lambda R} = \partial f^{\lambda\lambda}/\partial R$, where R denotes a stretching and λ a bending coordinate. In triatomics, stretching a bond eventually drops $f^{\lambda\lambda}$ to zero, thus the corresponding cubic derivatives are expected to be negative in the equilibrium structure, assuming that over the course of bond formation, $f^{\lambda\lambda}$ increases monotonically. Magnitudes and signs of many higher-order coupling constants are not at all straightforward to rationalize.

Displacement Coordinates

There are several requirements set forth for anharmonic force fields, which determine the best choice of vibrational displacement coordinates:

1. The force field expressed in the coordinate system chosen should be *isotope independent*. Only Cartesian and customary internal coordinates satisfy this desirable requirement, normal coordinates do not, because only Cartesian and the usual internal coordinates are strictly geometrically defined (i.e., no masses enter their definition).
2. The force field ought to be *diagonally dominant* at all orders, i.e., choice of the coordinates should lead to minimized interactions among them. Cartesian and normal coordinates are rectilinear by definition, whereas motion of the atoms of molecular systems happens along curved paths, i.e., the motion is curvilinear. Therefore, even when relatively small displacements are considered, the use of Cartesian and normal coordinates is disadvantageous.
3. The expansion of the potential should have *rapid convergence*. This can be achieved most easily with a careful choice of internal coordinates. However, this does not mean that a truncated power series expansion will behave correctly farther away from the reference geometry; the usual expansions may lead to convergence problems,[57] although to a different degree based upon the choice of the coordinates.
4. The coordinate system chosen should help the *transfer* and *comparison* of force constants between related molecules. Transfer of force constants from one molecule to another is facilitated, as a general principle, by the use of *local* coordinates, which extend to as few atoms as meaningful. Normal coordinates, besides being mass dependent, clearly do not satisfy this criterion but internal coordinates may. In accordance with the local-mode description of higher overtone bands,[58] anharmonicity in stretching distortions is concentrated mainly in individual bonds. Thus, using individual bond–stretch coordinates, the diagonal terms strongly dominate in the potential, facilitating transfer and comparison of (higher-order) force constants between related molecules.

In summary, (curvilinear) internal, often symmetrized, displacement coordinates are by far the best choice to represent anharmonic force fields. Then the question arises whether one could choose a best set of internal coordinates to represent the stretching and bending motions of molecular systems. For the representation of quadratic force fields, spectroscopists have long been using symmetry and local internal coordinates.[59] In quantum chemistry, the use of these coordinates, sometimes called natural internal coordinates,[60,61] received acceptance especially after automatic generation of these coordinates for most molecular systems was achieved.[61] For ring systems, removal of redundancies is facilitated by the use of natural internal coordinates. It is noted in passing that the use of redundant internal coordinates has become widespread[62] for quadratic force fields but not for higher-order ones.

A truncated expansion in the simple bond-stretching coordinate, R or $R - R_{\mathrm{e}}$, may result in energy values, which go to negative infinity for large R. The ensuing convergence problems will hinder the use of the PES if extended coordinate regions are to be sampled, for example, in variational nuclear motion computations.[63] Therefore, alternative expansion coordinates have been advocated,[64,65] including $1/R$, $\rho = (R - R_{\mathrm{e}})/R$, $2\,(R - R_{\mathrm{e}})/(R + R_{\mathrm{e}})$, $\{1 - (R_{\mathrm{e}}/R)^{-a-1}\}$, and $\{1 - \exp[-a\,(R - R_{\mathrm{e}})]\}$, where a is an adjustable parameter. It is straightforward to see that (a) the last expansion coordinate is closely related to the Morse potential; (b) the inverse stretching coordinate (R^{-1}), the Simons–Parr–Finlan coordinate (ρ),[64] and the subsequent expressions should have similar convergence characteristics; and (c) there are simple relations connecting some of these coordinates.[9] All these coordinates give faster convergence in the expansion of the potential than the traditional stretching coordinate.[63] Modifications of angle bending coordinates have also been proposed. The use of out-of-plane versus torsion coordinates in variational nuclear motion treatments may also affect the accuracy of the computed results.

As indicated in Table 1, there are two different normal coordinate systems. The mass-weighted one is determined from a harmonic force field via the first-order relationship $\mathbf{S} = \mathbf{L}\mathbf{Q}$, where the $\mathbf{L}$ matrix defines the transformation between the internal coordinates $\mathbf{S}$ and the normal coordinates

TABLE 2 | Number of Independent Force constants in Anharmonic Force Fields of Polyatomic Molecules Exhibiting Different Point-Group Symmetries

Terms	Linear XY_2 ($D_{\infty h}$)	Bent XY_2 (C_{2v})	XY_3Z (C_{3v})	X_6Y_6 (D_{6h})
Linear f^i	1	2	3	2
Quadratic f^{ij}	3	4	12	34
Cubic f^{ijk}	3	6	38	237
Quartic f^{ijkl}	6	9	102	1890
Quintic f^{ijkm}	6	12	249	12,031
Sextic f^{ijkmn}	10	16	562	69,448

Q. The dimensionless normal coordinates, q_r, are defined as $q_r = \gamma_r^{1/2} Q_r$, where $\gamma_r/\text{u}^{-1}\text{Å}^{-2} = 2\pi c\tilde{\omega}_r/\hbar = [(\tilde{\omega}_r/\text{cm}^{-1})/33.715258] = \lambda_r^{1/2}/\hbar$, $\tilde{\omega}_r$ are the harmonic vibration wavenumbers, and the λ_r values are the force constants in mass-weighted normal coordinates. Expansion of the potential in dimensionless normal coordinates is written as

$$V/hc = \frac{1}{2}\sum_r \omega_r q_r^2 + \frac{1}{6}\sum_{rst} \phi^{rst} q_r q_s q_t + \frac{1}{24}\sum_{rstu} \phi^{rstu} q_r q_s q_t q_t + \cdots \tag{5}$$

The term *harmonic* force field should be used only in a situation when the vibrations are completely separable and harmonic in each normal coordinate (i.e., the force field has no higher-order force constants in the normal coordinate representation); in all other cases, the second-order potential constants form part of a *quadratic* force field.

Unique Force Constants

As the related Hamiltonian needs to remain invariant under all the symmetry operations of the molecular symmetry group, the potential energy expansion, see Eq. (1), may contain only those terms which are totally symmetric under all symmetry operations. Consequently, a simple group theoretical approach, based on properties of the permutation groups, can be devised,[26,66,67] which yields the number and symmetry classification of the unique anharmonic force constants. The burgeoning number of constants at higher orders can be appreciated from the entries in Table 2. Note that the number of independent linear terms determines the number of independent structural parameters of a molecule.

It should also be pointed out that for molecules with degenerate vibrations, including electronic states of linear molecules not affected by the Jahn–Teller effect,[68] there are some *dependent* force constants, which have to be included in the power series expansion fixed by symmetry (e.g., for linear molecules, cylindrical symmetry results in simple relations among some of the bending force constants[69]). The inclusion of these constants in the force field is mandatory in order to make the expansion maintain correct symmetry properties.

Reference Structure

In theoretical prediction of molecular force fields, various choices can be implemented for the reference structures: (a) an optimized BO equilibrium (r_e^{BO}) geometry, obtained at the level of electronic structure theory used in the force field evaluation; (b) an experimental or empirical r_e or some form of a (ro)vibrationally averaged r_0, r_s, r_z, r_a, r_g, r_m, r_m^ρ, r_c, or r_α structure[70–72]; (c) an optimum geometry (r_e^{BO}) from a higher level of electronic structure theory; or (d) an empirically corrected theoretical geometry providing an improved estimate of r_e^{BO}. Conceptually, option (a) is preferred as evaluation of force constants at a point other than the optimized theoretical structure introduces nonzero forces on the atoms and the system is not at equilibrium. Nevertheless, moderate levels of electronic structure theory yield optimum geometric parameters containing substantial errors. In these cases, the corresponding force constant predictions are deteriorated merely as a consequence of the choice of a deficient reference geometry. This problem led to the recommendation of choice (b).[60,73,74] Unfortunately, for most polyatomic molecules of interest, accurate experimental (equilibrium) structures, consistent within a set of similar molecules, are simply not available.[71] Selection of the reference structure according to options (c) or (d) generally improves the accuracy of the theoretical anharmonic force field,[75,76] without establishing a dependence on experimental structure determinations.

Excellent agreement between experimental and calculated (anharmonic) force fields is meaningful only if the reference geometry chosen for the calculation coincides with the true (equilibrium) structure of the molecule, which is extremely difficult to determine experimentally.[71,77] As clear from the definition of the PES and its derivatives, a 'correct' force constant obtained at an incorrect reference geometry means that the nuclear–nuclear repulsion V_{nn} derivative is incorrect, and therefore the electronic energy derivative determined by the actual level of calculation must be in error as well. Thus, the following points need to be emphasized[76,78] about aspects of choosing a reference structure for the electronic structure computations of anharmonic force fields:

(1) The potential energy is composed of two sizeable terms which are opposite in sign and similar in magnitude, electronic (E_{e}) and nuclear–nuclear repulsion (V_{nn}) contributions. As the V_{nn} contribution and its derivatives can be calculated exactly and the E_{e} contributions and its derivatives only approximately, computation of force field elements becomes a rather unbalanced procedure.

(2) The E_{e} and V_{nn} contributions to the forces and the quadratic force constants almost cancel each other, whereas for the anharmonic force constants the V_{nn} derivatives become increasingly dominant. Thus, higher-order bond-stretching derivatives depend strongly on the reference structure at which they are evaluated. As the approximate electronic derivatives make smaller and smaller contributions to force constants of higher and higher order, anharmonic force constants can be calculated to higher accuracy than equilibrium structures or quadratic force constants, especially if the reference structure is accurate.

(3) For small reference bond length variations (δr_i), the percentage change in the predicted harmonic frequency at a given level of electronic structure theory is approximately $50(f^{iii}/f^{ii})\ \delta r_i$. Thus, for most simple molecules, even a small $\delta r_i \approx +0.002$ Å discrepancy gives rise to a frequency change of about -0.7%.[79]

Let us now concentrate on a force field expansion in Cartesian space, which can be the result of an electronic structure computation. When a Cartesian force field is used in a nonvariational vibrational analysis, one possibility for circumventing the effects caused by the linear terms (forces) in the expansion is to neglect the Cartesian forces. This procedure, however, must be considered invalid as the PES, upon which the analysis is based, is not rotationally invariant, resulting in the appearance of three nonzero 'rotational' frequencies. Rotational dependence of the local PES may be removed by projection techniques designed to construct rotationally invariant PESs without reference to any particular set of internal coordinates.[76,78] The form $\mathbf{P} = \mathbf{AB}$ of the first-order projection matrix employed for quadratic force fields is widely utilized, where $\mathbf{B}$ is the rectangular El'yashevich–Wilson $\mathbf{B}$ matrix,[59] whereas $\mathbf{A}$ is its generalized inverse. Higher-order projection protocols, most importantly the Cartesian projection scheme (CPS), have been developed[76] and modify the original Cartesian force fields at all orders.

If the anharmonic force field is evaluated at a nonstationary reference geometry in internal coordinates, the internal coordinate forces can be neglected and the vibrational analysis performed as if based on a stationary reference geometry. This procedure has been widely employed.[75] With the usual choices of internal coordinate systems, the results obtained in this way for semirigid molecules turn out to be rather accurate. In variational nuclear motion treatments, the forces could be kept but there is some evidence[63] that even in this case it is better to get rid of them.

In summary, it is often advantageous to choose a nonstationary reference structure for the evaluation of force fields. There exists no one, unique solution how to deal with the forces thus appearing in the expansion. In favorable cases, for example, for semirigid molecules, neglect of forces in a suitable internal coordinate system or using the CPS technique will lead to similar but not identical results. For systems having floppy vibrations or weak intermolecular interactions, it is perhaps best to avoid the use of nonstationary reference geometries during (anharmonic) force field studies.[78]

COMPUTATION OF ANHARMONIC FORCE FIELDS

Because of the concerted effort of a considerable number of electronic structure theorists, efficient techniques to compute analytic first and second derivatives exist for many wavefunction techniques, a partial list of important contributions is given in Refs 80–91. Beyond second order, analytic derivative techniques are available only for the simplest levels of electronic structure theory.[86] Therefore, it is a technical difficulty to obtain anharmonic force constants from low-order data. The two basic methods for determining derivatives of the PES numerically are least-squares fitting and the use of finite-difference expressions.[6,92–94] An unpleasant feature of both approaches is that the inherent uncertainties in the data set are magnified at higher orders.

Determination of anharmonic force fields through least-squares fitting from energy points alone represents a simple approach and amounts to the calculation of total energies at several nuclear configurations in which some coordinates have been displaced, whereas others are kept at their reference values. A polynomial surface is then fitted to the various energies, see, for example, Ref 92. The large number of parameters requires that the number of points along each coordinate be considerably larger than the degree of the polynomial used. Partial solutions to the problem that different combinations of energy points yield different force constants have been advocated: (a) calculations can be performed on points selected according to the roots of a Chebyshev polynomial thus facilitating interpolation and (b) averaging of the results obtained from different, appropriate selection schemes. Sophisticated approaches, such as the interpolative moving least-squares fitting method, have also been proposed to minimize the number of *ab initio* points required and the cost of the fitting as well as to allow the use of derivative information.[94]

To minimize errors of the numerical derivative approximations, it is preferable to employ central differences in the finite-difference formulas[92] when the basis functions depend on the perturbation, which they do for geometrical derivatives. A broad variety of such formulas follow by differentiation of appropriate collocating polynomials. Forces and diagonal quadratic force constants may then be determined from displacements along a single coordinate by, for example, the following three- and five-point central-difference formulas:

$$\begin{aligned} f^{i} &= (2\Delta_i)^{-1}(F_1 - F_{-1}) + O(f^{(iii)}) \quad \text{and} \\ f^{ii} &= \Delta_i^{-2}(F_{-1} - 2F_0 + F_1) + O(f^{(iv)}) \end{aligned} \tag{6}$$

or

$$\begin{aligned} f^{i} &= (12\Delta_i)^{-1}(F_{-2} - 8F_{-1} + 8F_1 - F_2) \\ &\quad + O(f^{(v)}) \quad \text{and} \\ f^{ii} &= \left(12\Delta_i^2\right)^{-1}(-F_{-2} + 16F_{-1} - 30F_0 \\ &\quad + 16F_1 - F_2) + O(f^{(vi)}), \end{aligned} \tag{7}$$

where Δ_i is the displacement along internal coordinate i, the Fs are total energies, their subscripts refer to positive (single) (e.g., F_1) or negative (double) (e.g., F_{-2}) displacements, and the last terms refer to truncation errors. The rapidly increasing complexity of the formulas with increasing number of points and decreasing formula error is obvious. The complexity of the formulas also increases for mixed derivatives. If analytic derivative information is available to a given order, all information could be employed to obtain certain derivatives from a reduced number of points or to check the precision of the determination of the anharmonic force field. In general, the F's of the finite-difference formulas presented may be either the total energies or its analytic first, second, third, and so on derivatives with respect to the geometric coordinates. In general, the use of finite differences is recommended over the use of least-squares fitting as this way less points are needed and higher precision can usually be achieved. A robust methodology based on computer algebra has been implemented.[95]

Numerical precision of computed anharmonic force fields depends on at least the following factors: (a) the precision of the optimized reference structure; (b) the precision of the calculated analytic data; (c) the truncation and round-off errors; and (d) the displacement sizes. Although, in general, sizeable errors are anticipated in approximate higher derivatives determined numerically, in careful anharmonic force field computations all error factors can be minimized straightforwardly.

Determination of Cartesian coordinates for a polyatomic molecule distorted by a specified amount along one or some of the non-Cartesian coordinates is not trivial. The simplest approach[96] in the case of curvilinear internal coordinates is based on the iterative application of the first-order equation connecting Cartesian, **X**, and internal, **S**, displacement coordinate sets according to

$$\mathbf{X}_{n+1} = \mathbf{X}_n + \mathbf{A}\,(\mathbf{S} - \mathbf{S}_n). \tag{8}$$

For usual displacement sizes, convergence can be easily accomplished in a few steps. The program INTDER[97,98] can perform the internal to Cartesian inversion using higher-order B tensors.

If analytic second derivatives are available and the normal coordinate force field is to be used only in a VPT2 calculation of spectroscopic constants, all normal coordinate force constants required can be determined[99] by a reduced number of simple finite-difference formulas utilizing displacements along single normal coordinates. If quartic force fields of larger molecular systems are needed in a spectroscopic analysis, this technique, although of limited utility in general, can be particularly advantageous.

TRANSFORMATION OF FORCE FIELDS

As in electronic structure computations derivatives of the total energy of molecular systems with respect to geometrical coordinates are obtained in Cartesian coordinates, transformation of these derivatives to coordinate systems of more practical use, for example, internal or normal coordinates, needs to be discussed.[69,97,100–102]

If two distinct sets of displacement coordinates are denoted by vector components r_i and q_r, a nonlinear transformation would take the general form,

$$r_i = \sum_r X_i^r q_r + \frac{1}{2}\sum_{rs} X_i^{rs} q_r q_s + \frac{1}{6}\sum_{rst} X_i^{rst} q_r q_s q_t + \frac{1}{24}\sum_{rstu} X_i^{rstu} q_r q_s q_t q_u + \cdots \tag{9}$$

The transformation coefficients evaluated at the reference geometry, $X_i^{rs\cdots}$, are the appropriate derivatives of r_i with respect to q_r.

When the X elements are used to transform the potential energy, V, from the **r** representation to the **q** representation, somewhat complex, nonlinear transformation equations are obtained involving sums over many permutations of the indices. The brace notation, detailed in Refs 76 and 97, can be used to cast the complex formulae in possibly the simplest form.

Because the molecular PES does not depend on the external variables (translation and rotation) of the system [thus, the BO PES depends upon $3N - 6(3N - 5)$ degrees of freedom for nonlinear (linear) molecules], the components of the Cartesian gradient can be determined via a linear, tensorial transformation of the internal forces alone,

$$V^r = \sum_i V^i B_i^r, \tag{10}$$

where V^r and V^i denote Cartesian and internal coordinate potential energy derivatives, respectively, the summation goes through the number of internal coordinates, and B_i^r are elements of the **B** matrix.[59] The higher-order transformation expressions arise by direct differentiation of Eq. (10). Closed analytic formulae for the transformation coefficients, collectively called **B** tensor elements, may be obtained by differentiating the relevant internal coordinates with respect to the Cartesian displacements, much the same way that the **B** matrix elements have been obtained.[59,97]

A simplified method exists[69,97] for setting up the required nonlinear coordinate transformations from curvilinear internal coordinates to simple normal coordinates. The transformation coefficients are called the **L** tensor elements and the transformation equation can be written in second order as

$$\phi^{rr} = \lambda_r = \sum_{ij} f^{ij} L_i^r L_j^r. \tag{11}$$

One convenient set of equations to calculate the elements of the **L** tensor[69] has been given for the five basic types of internal coordinates (stretch, bend, linear bend, out-of-plane, and torsion).[97]

QUALITY OF *AB INITIO* FORCE FIELDS

When trying to assess the accuracy of anharmonic force fields, it has to be realized that (ro)vibrational wavenumbers, quantities straightforwardly related to force fields, of semirigid molecules are determined mainly by diagonal terms in an internal coordinate force field. For example, in gaseous $H_2{}^{16}O$, the main contributions to the harmonic wavenumbers $\omega_1 = 3832$, $\omega_2 = 1648$, and $\omega_3 = 3942\,\text{cm}^{-1}$ come from the quadratic force constants f^{rr} and $f^{\alpha\alpha}$, providing contributions of 3879, 1676, and $3896\,\text{cm}^{-1}$, respectively.[77,103] Therefore, diagonal force constants can be determined rather accurately via simple models relating the experimental observables, the transitions, to structures and force fields (see, e.g., Ref 28). For off-diagonal force constants, especially at higher orders, theory provides the considerably more dependable values. The best force fields, harmonic or anharmonic, can be determined by a judicious combination of experimental and theoretical information.

There are several factors which influence the quality of *ab initio* force fields, whether harmonic or anharmonic, including (a) choice of the electronic Hamiltonian; (b) treatment of the many-body electron correlation problem; (c) selection of the one-particle basis set expansion; and (d) the reference geometry.[13,44,76] Although importance of the first three factors should be considered for almost all quantities determined by methods of electronic structure theory, the effect the choice of the reference geometry has on computed anharmonic force fields (and related spectroscopic quantities) involves subtle issues, explored above. The use of relativistic treatments[104,105] is necessary for molecules containing atoms beyond about nickel. For lighter atoms, relativistic effects are usually reasonably small so that they can be neglected completely or taken into account by a first-order perturbative treatment.[106,107] No further discussion on these two topics is offered here. In what follows, we concentrate on electron correlation and basis set effects. The rule of thumb is that basis set incompleteness tends to lengthen, whereas neglect of higher-order electronic excitations tends to shorten bonds. This almost in itself determines the quality of the calculated stretching force constants at higher levels of electronic structure theory.

A detailed discussion of the accuracy expected for force constants computed with Hartree–Fock (HF)[108–110] wavefunctions was first given in the 1960s.[73,74,111] As HF potentials often dissociate to the wrong limits, one might expect that they yield poor force constants even around equilibrium. This, however, is rarely the case. When HF theory is adequate, the error it introduces into force field predictions is usually systematic and causes these curves to give too short distances and overestimated force constants. Experience leads to the following general conclusions on the overall accuracy of force fields determined at the HF level with basis sets of at least medium *sp*(*d*) quality:

(1) Notwithstanding the sometimes gross overestimation of stretching force constants at theoretically optimized reference geometries, correlation effects on the intrinsic curvature of stretching potential curves are systematic and usually do not exceed 5% for single bonds and 10% for multiple bonds.[112]

(2) Changes in bond angles usually do not involve breaking or making of bonds. Therefore, HF wavefunctions should be able to describe the related anharmonicity. Overestimation of quadratic diagonal bending force constants is systematic, about 20%–30%. To improve the description of angle bendings, use of polarized basis sets is recommended. For bending force constants genuine correlation effects seem to be more important than for stretching constants.

(3) For the wide variety of coupling (off-diagonal) constants, the results are less systematic. The accuracy of their computation is nevertheless very good.

Overall, the electronic energy and its derivatives are typically predicted by HF theory to within a few percent in the strongly bonding region of PESs, a remarkable accuracy for this level of theory. Analytic fourth derivatives have been made available[88] at this simplest level of *ab initio* electronic structure theory.

As numerical differentiation techniques place severe requirements on the precision of the analytic data, among all the procedures developed to obtain electron correlation energies only those which by design result in (sufficiently) smooth potential surfaces should be employed for anharmonic force field calculations. The use of particular configuration interaction (CI) methods[113] based on perturbation expansions, techniques where configuration selection was introduced for the sake of computational efficiency, and density functional theory (DFT)[114,115] methods, without improving the numerical accuracy of their integral evaluations, should be discouraged. Nevertheless, certain DFT functionals offer considerable promise for anharmonic force field studies on larger molecular systems.[46,47,116,117]

Some correlated electronic structure methods employed with small basis sets are inappropriate for the provision of the underlying structure and the force field because the imbalance of basis set and correlation errors creates a propensity for the overestimation of bond lengths, resulting in greatly deteriorated force field predictions. For many systems, coupled cluster (CC) wavefunctions, for example, with single and double excitations (CCSD),[118] constructed with polarized basis sets of moderate size constitute a counterexample, as basis set incompleteness and the neglect of higher-order excitations tend to advantageously cancel in geometric structure determinations, leading to increased apparent accuracy in the force fields.

Well defined variational (CI-type),[113] perturbational (*n*th-order Møller–Plesset, MP*n*),[119] and CC techniques,[120] including the gold standard CCSD(T) method,[121] have all been employed to determine anharmonic force fields. Important conclusions of these studies[24–31,33–36] include: (1) Near equilibrium, the correlation energy is a low-order function of the bond distances, even a linear approximation is meaningful. (2) For open-shell species, spin contamination can significantly deteriorate results if an unrestricted HF reference function is used. Therefore, use of procedures based on restricted open-shell reference functions is recommended. (3) Correlated methods converge much slower with respect to basis set size than HF methods. Thus, rather large basis sets, of at least *spdf* quality, are required to obtain adequately converged force fields, especially at the quadratic level.

As usual, the atom centered, Gaussian basis set selected for an anharmonic force field computation should be sufficiently complete to allow a reasonably good description of the wavefunction and moderate in size so that larger systems of interest could be handled at an acceptable computational cost. In case of anharmonic force field studies, the computational cost can be substantial either in the case of a fully analytic calculation or if calculations are carried out at a large number of displaced geometries. In systematic studies of molecular families, it is probably worthwhile

TABLE 3 | Selected Anharmonic Force Constants of $H_2{}^{16}O$ Taken from the Literature[1]

Term	CVRQD (Ref 103)	CCSD(T)_FC/aug-cc-pVTZ (Ref 31)	Empirical (Set III, Ref 31)	HMS (Ref 69)
r_{ref}	0.957 854 Å	0.95843 Å	0.95843 Å	0.9572 Å
Θ_{ref}	104.500°	104.44°	104.44°	104.52°
f^{rr}	8.460	8.493	8.456	8.454
$f^{\alpha\alpha}$	0.703	0.697	0.708	0.709
$f^{rr'}$	−0.103	−0.089	−0.115	−0.101
$f^{r\alpha}$	0.258	+0.260	0.277	0.219
f^{rrr}	−58.68	−58.90	−58.49	−59.40
$f^{\alpha\alpha\alpha}$	−0.71	−0.68	−0.83	−0.88
$f^{rr'\alpha}$	−0.51	−0.50	−1.02	−0.40
f^{rrrr}	362.6	365.3	366.0	384
$f^{\alpha\alpha\alpha\alpha}$	−0.21	−0.33	−0.21	−0.1
$f^{rr\alpha\alpha}$	−0.688	−0.16	−0.24	−1.4
f^{rrrrr}	−2398.0	−2429.1	–	–
f^{rrrrrr}	18157.0	16855.6	–	–
$f^{rrr'r'r'}$	68.5	−44.3	–	–

[1] Units of the force constants are consistent with energy measured in aJ, distances in Å, and angles in radian. The reference geometry about which the force field was expanded is given by parameters r_{ref} and Θ_{ref}.

choosing a basis set with which results have been obtained for similar species.

In order to approach chemical accuracy for equilibrium structure and force field predictions, it seems necessary to include at least *f*-type functions in the basis set for 'heavy' atoms and usually *d*-type functions for hydrogen. The use of smaller basis sets inevitably leads to less accurate predictions, especially with highly correlated wavefunctions. Correlation consistent[122] and ANO[123] basis sets offer results of similar quality. It is not relevant any more that cost of the computation of integrals based on the former choice is significantly less. Adequate description of multiple bonds, especially triple bonds, requires considerably more extended basis sets than that of single bonds. Another difficulty is the description of atoms with high electronegativity (like O and F), in which case the use of diffuse functions should be considered.

Advances in the continuing development of quantitatively accurate *ab initio* methods have revealed the necessity of a full understanding of the consequences of the inclusion of core correlation on calculated force fields. It has been found[79,124] that (a) single and multiple bonds of diatomic molecules comprised of first-row atoms become shorter by about 0.001 and 0.002 Å, respectively; (b) the *direct* effect of core correlation, that is, under the constraint of a fixed internuclear distance, core correlation decreases the quadratic force constant such that the frequency is lowered; (c) core correlation decreases all higher-order force constants as well, bringing them to better agreement with experimentally determined values. Still, if core correlation is considered in a conventional, phenomenological sense as the difference between the harmonic frequency values for all-electron and partial-electron treatments, the core correlation can be said to increase the harmonic frequency, in accord with the change in r_e.

Finally, it seems worth giving at least one example in tabular form demonstrating numerically what was described above. The anharmonic force field of the water molecule has been determined at many levels of electronic structure theory employing various reference geometries (e.g., Refs 21, 31, 81, and 103 and references therein) as well as empirically (e.g., Refs 31 and 69). The ultimate quartic force field of $H_2{}^{16}O$ was determined by numerical differentiation of an exceedingly high quality composite *ab initio* PES denoted CVRQD.[8,103] The results are summarized in Table 3.

APPLICATIONS OF *AB INITIO* FORCE FIELDS

As anharmonic force fields provide an approximation to the true PES of a molecule, they can be employed in all modeling studies based on the concept of a PES. Some applications are commented here.

The relation of certain *spectroscopic constants* to elements of the anharmonic force field is indicated in Table 4. Anharmonic force fields, whether employed in perturbative or variational nuclear motion techniques, lead to information about the

TABLE 4 | Relation of Spectroscopic Constants to Force Fields

Terms	r_e	f^{ij}	f^{ijk}	f^{ijkl}
Rotational constant $B_e{}^{\alpha}$	+			
Harmonic vibrational wavenumbers $\tilde{\omega}_r$	+	+		
Quartic centrifugal distortion constants D_e	+	+		
Coriolis constants $\xi_{rs}^{(\alpha)}$	+	+		
Vibr. dependence of B, $\alpha_r^{(\alpha)}$	+	+	+	
Cubic (Fermi) resonance constants φ_{rrs}	+	+	+	
Sextic centrifugal distortion constants H	+	+	+	
l-Doubling constant $\bar{q}_t$	+	+	+	
Vibrational anharmonicities χ_{rs}	+	+	+	+
Quartic resonance $K_{rs;tu}$	+	+	+	+
Anharmonic constant $\chi_{l_t l_{t'}}$	+	+	+	+

assignment of low- and high-resolution rovibrational spectra, particularly for vibrational band origins not too far from the ground state. Vibrational anharmonicity also affects the transition intensities through the mixing of vibration–rotation wavefunctions.

In statistical theories of chemical *reaction rates*, a central role is assumed by the density of vibrational states.[125,126] The accurate *a priori* determination of this density is a formidable challenge at high energies. If direct count of states based on a harmonic model is unsatisfactory, an anharmonic model is the next level of approximation. For small molecules, this model works surprisingly well.[5] Nevertheless, discrepancies observed between direct state counts and experiments[127] suggest that at high energies still better methods need to be employed.

The nature of energy flow, in other words *intramolecular vibrational energy redistribution* (IVR),[128,129] within polyatomic molecules is an important factor controlling chemical dynamics. In many experimental IVR studies, for example, Refs 130–132, a high vibrational state is prepared before photolyzing the excited molecule. The dissociation yield depends on the degree of mode mixing in the intermediate state prepared. Mode mixing, in turn, is determined and visualized by appropriate elements of the anharmonic force field.

Molecular properties are often affected significantly by the vibrations and rotations of molecules.[70–72,133,134] It must be stressed that in a careful theoretical study, both nuclear motions should be considered. *Rotational–vibrational averaging* can be accomplished straightforwardly via variational nuclear motion computations if an accurate representation of the molecular PES is available. Around equilibrium position(s), the use of anharmonic force fields is very convenient, as well as the use of simple perturbative expressions. Averagings will lead to, for example, interconversions of the many distance types encountered in structural studies.[70,71] Consequently, the use of anharmonic force fields in accurate structural studies of small molecules has a long history.[70,133] Furthermore, a relationship between stretching force constants (anharmonic frequencies) and the corresponding bond length has been established for a long time,[135–137] and in certain cases,[136,137] it is still one of the most accurate methods to determine bond lengths.

Thermodynamic quantities can also be predicted with an accuracy approaching or even surpassing that of relevant experiments if the harmonic approximation is relaxed and an anharmonic force field is used to represent the PES of the molecule.[138]

CONCLUSIONS

Experimental information alone is insufficient to uniquely determine the anharmonic force fields of polyatomic molecules. As accurate anharmonic force field representations of PESs are useful in many branches of physical chemistry, force fields obtained from electronic structure computations are of considerable importance and utility.

The precision of anharmonic force fields does not deteriorate if the force field up to quartic terms is determined from well selected, precise energy points. For larger polyatomic systems with a large number of constants, either fully analytic determination of the force field is recommended (at present this can be accomplished up to quartic terms only at the HF level of theory) or information from analytic second derivatives should be employed.

The overall accuracy of calculated anharmonic force fields is as follows: (1) At a fixed reference geometry, most calculated cubic and quartic force constants show surprisingly small variation with respect to basis set extension and treatment of electron correlation. Even results obtained at the HF level are accurate, their error is systematic and rarely exceeds 10% if determined at a correct reference structure. (2) Particularly accurate *ab initio* force fields can be obtained if methods incorporating a large portion of the electron correlation energy with extended basis sets are used to evaluate these constants. Even small basis set correlated-level electronic structure computations can account for the highly structure-sensitive nondynamical electron correlation. (3) A substantial part of the discrepancy between force constants calculated at reference geometries stationary at the given level of theory and force constants obtained from experiments comes from the differences in the underlying geometries. Shifting the theoretical reference structure close to the true equilibrium geometry results in force constants which are usually in dramatically better agreement with their experimental counterparts. (4) Some of the higher-order force constants determined experimentally (especially the quintic and sextic ones, but in many instances the off-diagonal quartic ones, as well) do not seem to have physical significance, that is, they are not directly correspondent with the associated derivatives of the PES. For these constants, values from electronic structure theory should be considered to be more accurate. The best force fields can be determined from a judicious combination of experimental and computed information.

An obvious question at this point is why the usual anharmonic force fields include cubic and quartic but not higher-order terms. Although cubic terms are larger, they contribute only in the second order of VPT, whereas the smaller quartic terms contribute in first order. Thus, the magnitude of the contribution of cubic and quartic force fields to vibrational energy levels is fairly similar (higher-order force constants contribute in higher orders of perturbation theory). Furthermore,[139] analytic solution of the one-dimensional Morse-potential problem results in the same relation for energy levels as an approximate calculation based on VPT2 and truncation of the expansion of the Morse potential at the quartic term. This suggests that the simple VPT2 scheme is considerably more accurate than otherwise expected.

Finally, an obvious shortcoming of (truncated) anharmonic force fields must be emphasized. Anharmonic force field approximations to PESs do not have accurate asymptotic (dissociation) behavior, even if improvements are made on the choice of the expansion coordinates. Thus, force field-type expansions should not be employed, for example, for studies on highly excited (ro)vibrational states.

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