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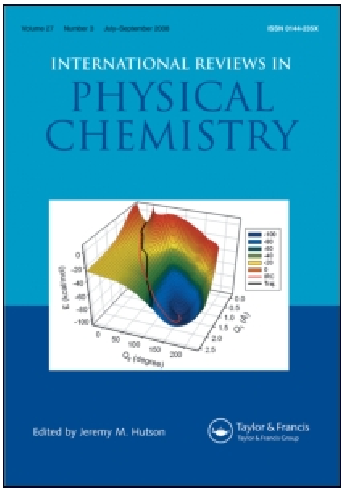

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Analytic second derivatives in high-order many-body perturbation and coupled-cluster theories: computational considerations and applications

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The history of analytic first- and second-derivative methods in quantum chemistry is discussed, with special emphasis given to approaches that are associated with electron correlation treatments based on many-body perturbation theory (MBPT) and the coupled-cluster (CC) approximation. The computational requirements of recently developed analytical second derivative methods for high-order MBPT and CC methods are discussed in detail and compared with those associated with finite-difference procedures. Applications of these techniques to the calculation of anharmonic force fields used to deduce equilibrium geometries and fundamental vibrational frequencies for polyatomic molecules are reviewed.

1. Background

Analytic derivative methods are arguably the most important tools available to the computational chemist for studying the structure, potential energy surface and spectroscopy of molecules. While the importance of such calculations was recognized very early by Bratoz [1], Pulay was the first to plough this fertile area of research. Although it is obvious that analytic derivatives are more accurate than those obtained by numerical differentiation, Pulay [2] was able to demonstrate that the first derivatives of the self-consistent field (SCF) energy are also obtained most efficiently by analytic procedures. After developing a computer program to perform gradient calculations, Pulay [3] and collaborators used a mixed analytical–numerical method (dubbed the 'force method') based on numerical differentiation of analytic derivatives to study the harmonic force fields of a wide range of molecules. Analytic first derivatives led to a revolution in the scope of practical application studies. In particular, many of the tasks taken for granted today (geometry optimizations, harmonic frequency calculations and transition state searches for polyatomic molecules) became routinely possible for the first time.

The remarkable feature that numerical evaluation of derivatives can be considerably more expensive than analytic calculation is a consequence of the so-called $2n+1$ rule of perturbation theory. It is possible to show that the $(2n+1)$th derivative of the energy with respect to some perturbation (nuclear displacement, electric field, etc.) can be expressed entirely in terms of derivatives of the wavefunction through order n and all derivatives (up to order $2n+1$) of the Hamiltonian. Hence, only the first derivatives of the one-electron and interelectronic repulsion integrals with respect to the perturbations must be calculated to obtain the energy derivatives. For

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one-electron perturbations, the cost of this extra step is negligible; for two-electron perturbations such as nuclear displacements the cost is generally comparable with the SCF calculation itself. Therefore, SCF gradient calculations require roughly twice the computer time need to evaluate the energy. Since the number of non-vanishing differentiated one- and two-electron integrals does not scale with the number of nuclear displacements considered (for any order of differentiation), no step involved in a SCF gradient evaluation has such a dependence. It must be emphasized that the relative cost of analytic gradient and energy calculations is constant, whether one considers a diatomic molecule or a larger system such as *p*-dinitrobenzene. In contrast, the cost of numerical differentiation of the energy necessarily scales with the number of atoms. Hence, although just two energy calculations suffice for the diatomic[1], 16 are needed for all non-vanishing and symmetry-distinct derivatives in the latter example. While there is no advantage apart from accuracy in calculating the derivative analytically for the diatomic molecule, numerical evaluation of the gradient for *p*-dinitrobenzene requires about an order of magnitude more computer time.

From the previous paragraph, it should be clear that the advantages of analytical derivative evaluation are not restricted to the SCF level of theory. Indeed, the $2n + 1$ rule can be applied to any quantum chemical method that involves wavefunction optimization. The insatiable demand for greater accuracy and the astounding improvements in computer technology in the late 1970s and 1980s provided the impetus for a great deal of work in which analytic derivative methods were developed for approaches that treat electron correlation effects. The first success in this area was reported by Pople *et al.* [4] in 1979, who implemented first derivatives for the simplest electron correlation treatment, that is second-order many-body perturbation theory (MBPT(2)) [5].

At the correlated level of theory, the wavefunction is parametrized by the basis set expansion coefficients of the molecular orbitals, and a set of amplitudes that serve to weight the contribution of various Slater determinants in the electronic wavefunction. While the $2n + 1$ rule guarantees that it is possible to eliminate derivatives of wavefunction parameters even when the energy is not stationary with respect to first-order variation of them, it was not immediately clear how this might be done in practice. For MBPT(2), Pople *et al.* [4] explicitly solved for the perturbed molecular orbitals and found that the first-order amplitude parameters could be eliminated in a trivial way. The former procedure involves solution of the coupled–perturbed Hartree–Fock (CPHF) equations [6, 7], and its cost is negligible when compared with the other requirements of a correlated calculation. While configuration interaction (CI) methods [8] are defined in such a way that the energy is stationary with respect to variation of the wavefunction amplitudes, methods based on MBPT and the coupled-cluster (CC) approximation [9–12] (where wavefunction amplitudes will be designated by **T**, which is assumed to comprise contributions of various order when appropriate for MBPT calculations) do not share this feature. In the MBPT and CC methods, however, all contributions to the energy derivative

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[1] In order to achieve acceptable accuracy, it is customary to use double-sided numerical differentiation, that is $\mathrm{d}f/\mathrm{d}x|_{x_0} \approx \frac{1}{2}\delta^{-1}[f(x_0 + \delta) - f(x_0 - \delta)]$, where δ is some small displacement.

that involve amplitude derivatives $\partial \mathbf{T}/\partial\chi$ have the general mathematical structure

$$\frac{\partial E}{\partial \chi} \Leftarrow \mathbf{aM}^{-1} \cdot \mathbf{b}^{\chi}, \qquad (1)$$

in which evaluation of $\mathbf{M}^{-1}\mathbf{b}^{\chi}$ gives the corresponding $\partial \mathbf{T}/\partial\chi$ amplitudes and $\mathbf{a}$ is independent of the perturbation [13–16]. The matrix $\mathbf{M}$ is much too large to be inverted explicitly, and iterative procedures are therefore required. Inspection of equation (1) shows that there is an option of evaluating several sets of $\partial \mathbf{T}/\partial\chi$ amplitudes (with respect to all perturbations) and contracting the solution vectors with $\mathbf{a}$, or solving just one linear equation, $\mathbf{z} = \mathbf{aM}^{-1}$ and taking the dot product of $\mathbf{z}$ with all $\mathbf{b}^{\chi}$. For the MBPT, this issue does not arise (the matrix $\mathbf{M}$ is usually diagonal), but it is important in the context of CC theory. At this level, evaluation of either a specific $\mathbf{M}^{-1}\mathbf{b}^{\chi}$ or $\mathbf{aM}^{-1}$ costs roughly the same as an energy calculation; the dot products require essentially no time at all. Hence, the second strategy mentioned above is preferred. This general approach was apparently first used in quantum-mechanical computations by Sternheimer and Foley [17] in 1953 and somewhat later by Dalgarno and Stewart [18] but was introduced into quantum chemistry three decades later by Handy and Schaefer [19] to remove the dependence of CI derivatives on the perturbed molecular orbitals. In an important subsequent paper, Adamowicz *et al.* [20] applied this technique to the problem of eliminating all $\partial \mathbf{T}/\partial\chi$ contributions from analytic derivative expressions in CC theory. The corresponding solution vector is commonly referred to as $\mathbf{\Lambda}$ in the literature [16, 21]. A somewhat different perspective on CC gradient theory is possible, in which the energy is given as an eigenvalue to a non-Hermitian similarity transformed Hamiltonian matrix[2]. In this approach, $\mathbf{\Lambda}$ arises in a natural way as the left eigenvector of this matrix and the stationary nature of the eigenvalue problems can then be used to simplify the gradient formulation. Hence, it is quite convenient to regard the $\mathbf{\Lambda}$ amplitudes as an additional (but inessential) set of wavefunction parameters for CC and MBPT (where analogous quantities can be defined at each order) and we shall do so for the remainder of this article.

Outlined above are many of the significant advances that have led to the ready availability of analytic first derivative methods for essentially all quantum-chemical methods. For variational methods, analytic derivatives have been implemented for SCF [2], CI [23, 24], multiconfigurational self-consistent field (MCSCF) [25, 26] and MCSCF-based CI procedures [27]. Non-variational methods based on the MBPT and CC theory are more often used in quantum-chemical studies than CI approaches, however, and it seems clear that the coupled cluster singles plus doubles with perturbative triples (CCSD(T)) treatment of electron correlation [28] is the *de facto* method of choice when highly accurate results are desired. As seen in table 1, analytic gradient methods are available for CCSD(T) as well as for all other levels of MBPT and CC that are commonly used in chemical applications[3].

SCF second derivatives were first implemented efficiently by Pople *et al.* [4] and described in their classic 1979 paper. At this level of theory, it turns out that analytic evaluation is considerably more efficient than numerical differentiation of analytic derivatives. While it is true that the first derivative of all wavefunction parameters

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[2] For a discussion on this point, see [22].

[3] For reviews, see [11] and [29].

Table 1. Availability of analytic first- and second-derivative implementations for MBPT and CC methods as of 1994: SDQ–MBPT(4), fourth-order many-body perturbation theory exclusive of triple excitations; CCD coupled cluster doubles; QCISD, quadratic configuration interaction singles plus doubles; CCSD, coupled cluster singles plus doubles.

Method	Asymptotic cost	First derivatives	Second derivatives
MBPT(2)	N^5	X	X
MBPT(3)	N^6	X	
SDQ–MBPT(4)	N^6	X	
CCD	N^6	X	
QCISD	N^6	X	
CCSD	N^6	X	X
MBPT(4)	N^7	X	
CCSD+T(CCSD)	N^7	X	
CCSD(T)	N^7	X	
QCISD(T)	N^7	X	
CCSDT–1	N^7	X	
CCSDT–2	N^7		
CCSDT–3	N^7		
CCSDT	N^8		
CCSDTQ	N^{10}		

must be determined in an analytic second-derivative calculation, solution of the corresponding CPHF equations is an insignificant computational step even when a fairly large number of perturbations is considered. Moreover, storage of the differentiated molecular orbital coefficients does not represent a practical problem even when very little disk space is available. Since solution of the CPHF equations does not represent a rate-limiting computational step, the cost of analytic SCF second-derivative calculations does not scale with the number of perturbations. Consequently, it is clearly preferable to any sort of numerical procedure and therefore is used almost exclusively in practice.

With regard to analytic second derivatives at the correlated level, the situation is qualitatively different from that associated with first derivatives. Analytic calculations of harmonic force constants and other second-order properties are rarely found in the literature for correlated methods other than MBPT(2) [30] and MCSCF [31]. Table 1 shows that analytic second derivatives had been implemented for only two non-variational treatments of electron correlation up to 1994. MBPT(2) second derivatives were developed simultaneously by the Cambridge and Gainesville groups in 1984 [32, 33] and later implemented in a number of commercially available program packages. However, it appears that only a single application calculation was reported with the first implementation of CCSD [34] second derivatives, programmed 10 years ago in a joint effort of the Aarhus and Georgia groups [35]. Among variational methods, CI second derivatives have been implemented [36] but are seldom used in practice. From the above, it is easy to see that no advances having a significant impact on chemical applications were made in the field of analytic second-derivative calculations for more than a decade.

There are three primary reasons why development of analytic second derivatives for correlated methods advanced much more slowly than that of first derivatives. First, the necessary evaluation of differentiated wavefunction parameters is now a rate-determining computational step and the cost of these calculations therefore scales with the number of perturbations. When one remembers that analytic first derivative evaluation has no such dependence, an argument can be made that the efficiency of calculating second derivatives by numerical differentiation of first derivatives (the force method) is comparable with that of analytic evaluation at the correlated level. Second, most formulae worked out for analytic second derivatives have the property that interchanging the positions of the perturbations α and β leaves the equation for $\partial^2 E/(\partial\alpha\,\partial\beta)$ unchanged. A consequence of this 'symmetric' property is that it is necessary either to store derivative wavefunction parameters for all perturbations simultaneously or to accept a computational cost that scales with the square of the number of perturbations. In contrast with gradient calculations, which require only about twice the disk storage of the corresponding energy evaluation[4] (there is no dependence on the number of perturbations), the first option ultimately imposes limitations on the size of systems that can be treated and was especially relevant in the 1980s and early 1990s (when 1 Gbyte of disk space was considered a luxury); the second option is clearly unacceptable. The final reason for the stagnated development of correlated second-derivative methods is simply that these approaches are complicated, both in the derivation of the equations and in the logic of a computer program that is needed to solve them. While quantum chemists have never allowed complexity to be the sole barrier to progress, the two practical considerations discussed above provided a sufficiently large incremental barrier that little effort was made in this area for many years.

In spite of the issues raised in the preceding paragraph, there are several areas of application in which analytic second derivatives are useful. An extreme example is provided by magnetic properties, particularly nuclear magnetic resonance (NMR) chemical shifts which represent perhaps the most important spectroscopic observable in organic chemistry. Elements of the chemical shielding tensor are given by second derivatives of the energy with one class of perturbations comprising the three magnetic field components and the other $3N$ (N is the number of atoms) are the nuclear magnetic moments. Since the magnetic field is a formally imaginary perturbation, any sort of numerical evaluation of magnetic properties requires the calculation of wavefunctions parametrized by complex numbers [37, 38]. Because the number of quantities that must be calculated and processed is doubled, such calculations are necessarily more expensive. Moreover, few program packages support complex wavefunctions, especially at the high-order MBPT and CC levels, where the cost of energy evaluation is greater than that incurred when only real wavefunction parameters are involved [39].

A second area is the determination of anharmonic force fields and other types of higher-order property. In order to go beyond the usual comparisons with experiment used in quantum chemistry that are based on harmonic vibrational frequencies, rotational constants determined from moments of inertia of the equilibrium structure

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[4] This statement applies to CC theory and MBPT at third and higher orders. MBPT(2) is a special case and the required disk space is considerably less. In the remainder of this article, use of the term 'high-order' MBPT will be used to refer to all MBPT methods beyond (and exclusive of) MBPT(2).

and so on, it is necessary to carry out such calculations. While it should be mentioned that the use of high-level CC correlation methods for calculations of this type was pioneered by Lee, Taylor, Martin and their associates[5], it is undeniable that the purely numerical procedures used in their work scale less favourably with the size of the system than those based on numerical differentiation of analytic second derivatives. To predict positions of vibrational levels with spectroscopic perturbation theory [42], it is necessary to evaluate fourth derivatives of the energy. Within a purely numerical procedure, the number of required energy points must increase with the fourth power of the number of coordinates, while the cost of evaluating the entire quartic force field scales only with the third power when the calculation is based on numerical differentiation of either analytic gradients or analytic second derivatives. Since the accuracy of quartic force constants calculated as numerical second derivatives of analytic harmonic force constants is higher than of those obtained by numerical differentiation of analytic gradients, the former option is preferable. In fact, it has been stated explicitly in the literature that 'the determination of complete quartic force fields for larger molecules is not feasible without analytic higher-order derivative methods' which (at that time) 'are not available in most cases' [43].

For the past 5 years, our groups have been actively engaged in the development and implementation of analytic second-derivative methods for high-order MBPT and CC methods, and in their application to problems of the sort mentioned above. The remainder of this paper is devoted to a discussion of these methods and some of the chemical applications for which they have thus far been used. In the next section, a brief sketch is given about how some of the problems mentioned earlier have been overcome in our approach as well as a fairly comprehensive discussion of the computational requirements associated with our analytic second-derivative implementation. We have chosen to limit the number of equations and mathematical detail in favour of a more general description that covers most of the major issues involved in these calculations. Following that, a description is given of how these methods are used to calculate anharmonic force fields and some pertinent application studies are reviewed.

2. Computational aspects

2.1. *Asymmetric strategy for second derivatives*

In the early 1990s, it was realized that the disk space and computational scaling problems associated with correlated analytic second derivative calculations could be avoided in calculations of NMR chemical shifts [44]. For calculations of the chemical shielding tensor (which is diagonalized to obtain the chemical shifts), analytical second derivatives have turned out to be particularly useful [38, 45]; all quantities encountered in the procedure are either real or purely imaginary. Hence, real arithmetic can be used throughout the program (with a caveat that imaginary quantities are given by antisymmetric matrix representations), which avoids the problem associated with processing complex wavefunction parameters. Second, all strategies for computing NMR chemical shifts at the SCF level are based on an equation for the second derivative that is not symmetric in the sense that interchange of the magnetic field and nuclear magnetic moments changes the appearance of the

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[5] For representative examples, see [40, 41] and references therein.

expression [38, 45–47]. Such 'asymmetric' second-derivative formulae can always be derived by taking the optimal form of the first-derivative expression (in which perturbed wavefunction parameters do not appear) and differentiating this with respect to the second class of perturbations. The resulting expression takes the generic form

$$\frac{\partial^2 E}{\partial\alpha\,\partial\beta} = \mathbf{D}\frac{\partial^2 \mathbf{H}}{\partial\alpha\,\partial\beta} + \frac{\partial \mathbf{D}}{\partial\beta}\frac{\partial \mathbf{H}}{\partial\alpha}, \tag{2}$$

where **D** represents effective one- and two-particle density matrices specific to the method used[6] and is a function of the unperturbed wavefunction parameters (molecular orbital coefficients and **T** and **Λ** amplitudes).

At the correlated level of theory, significant practical advantages can be achieved if β is associated with the magnetic field perturbation (there are three components) and α with the nuclear magnetic moments ($3N$, where N is the number of atoms). With this choice, it is necessary to solve for only three sets of perturbed wavefunction amplitudes, with the consequence that the computational time required for these calculations does not exhibit a dependence on the size of the molecules apart from that associated with the basis set. Even though storage of three sets of perturbed amplitudes is unlikely to pose a problem, equation (2) can still be evaluated efficiently if only one set of amplitudes is stored at a given time. For all methods beyond MBPT(2), the cost of calculating the perturbed density scales with at least the sixth power of the basis set size, while that associated with derivative integral evaluation scales only with the fourth power. This qualitatively different computational dependence can be exploited by storing the perturbed density on disk for a particular perturbation and then contracting it with derivative integrals (which are never written to disk but rather processed as they are calculated) for all perturbations.

Calculations of NMR shifts at the MBPT(2) level were first carried out using the strategy sketched above [44, 49]. Implementation at the MBPT(3), SDQ–MBPT(4), MBPT(4), QCISD [50], CCD [51, 52], CCSD [34] and CCSD(T) [28] levels followed and were reported within a 3 year period in the middle of this decade [48, 53–55]. Because problems associated with numerical calculations of NMR chemical shifts had been sufficient to prevent any previous high-order MBPT and CC calculations, these pioneering studies gave the first glimpse of how electron correlation effects described by the popular MBPT and CC methods affect this critically important chemical property.

It is important to realize that the strategy of storing only one set of perturbed amplitudes for evaluating the second contribution to equation (2) is not restricted to NMR shift calculations (or any other property for which α represents a class of perturbations that comprises only three components). In particular, one can apply the same approach to the calculation of harmonic force constants. While it is true that such a calculation still requires the solution of perturbed amplitude equations for each independent nuclear motion coordinate and therefore has a computational cost that scales with the number of atoms in the system, the amount of disk space needed is only about twice that of a gradient calculation. Despite this, there is an undesirable feature of this approach which warrants discussion. A formula for

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[6] See [48] for explicit definitions.

MBPT and CC second derivatives that is symmetric with respect to interchange of α and β can be written in the general form

$$\frac{\partial^2 E}{\partial\alpha\,\partial\beta} = \mathbf{D}\frac{\partial^2 \mathbf{H}}{\partial\alpha\,\partial\beta} + \left(\frac{\partial \mathbf{D}}{\partial\beta}\right)_{\mathbf{\Lambda}}\frac{\partial \mathbf{H}}{\partial\alpha} + \left(\frac{\partial \mathbf{D}}{\partial\alpha}\right)_{\mathbf{\Lambda}}\frac{\partial \mathbf{H}}{\partial\beta} + \left(\frac{\partial^2 \mathbf{D}}{\partial\alpha\,\partial\beta}\right)_{\mathbf{\Lambda}}\mathbf{H}. \tag{3}$$

The subscripts on the partial derivatives have the same sense as in thermodynamics; contributions that include differentiated $\mathbf{\Lambda}$ amplitudes are omitted. Hence, there is a definite computational advantage to the symmetric approach; only the linear equation that defines the $\partial\mathbf{T}/\partial\chi$ amplitudes must be solved for each perturbation χ since the corresponding $\partial\mathbf{\Lambda}/\partial\chi$ amplitudes are not needed. It is the fourth term of equation (3) that is somewhat problematic. There are essentially two options that can be exercised to evaluate it, and neither is entirely satisfactory. The first is based on the aforementioned simultaneous storage of all differentiated wavefunction parameters. While not a serious problem nowadays for most CCSD calculations[7], it does eventually represent a constraint. The second choice is to store just one set of perturbed amplitudes, followed by calculation of those corresponding to all other perturbations and contracting them 'on the fly' with the stored amplitudes, a process that must be repeated for all perturbations. This results in a computational dependence on the square of the number of atoms, which is a most unsatisfactory situation.

Despite these qualifications, it is our belief that the asymmetric approach based on equation (2) represents a highly practical and generally useful method for second-derivative evaluation at highly correlated MBPT and CC levels of theory. First, it can be applied quite easily to the calculation of all second-order properties, whether or not the two classes of perturbation are the same. When they are not, it is certainly preferable to the symmetric approach since fewer sets of perturbed amplitudes need to be evaluated. For force constants, polarizabilities and other such properties, it is less efficient with regard to computer time at the CCSD level and an implementation of the symmetric approach might be warranted. However, some of our current research efforts are directed towards analytic second derivative calculations at the CCSD(T) level of theory where the fourth term of equation (3) represents a serious problem indeed. Another reason for preferring the generally applicable asymmetric strategy is that accurate calculations of molecular properties require some treatment of triple excitation effects. Accordingly, the CCSD(T) method is heavily used in practice. In analytic second derivative evaluation at this level of theory, the energy contribution due to triple excitations is treated separately from the CCSD correlation energy. There is a clearly optimal method for obtaining the second derivative of the triples energy, which usually represents a significant fraction of the overall computational time. Hence, the question of whether the asymmetric or symmetric strategy is followed for the CCSD contribution becomes a less important issue with regard to computer time [56]. Finally, use of equation (2) allows some additional second-order quantities to be evaluated for negligible cost. For example, in a force constant calculation, one can simply augment the list of perturbations represented by α in equation (2) by the electric field. Since the calculation of the dipole integrals (corresponding to $\partial\mathbf{H}/\partial\alpha$) requires essentially no computer time, the full set of dipole

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[7] For a calculation on a molecule containing 12 atoms and 40 electrons described by 200 basis functions in C_s symmetry, the storage requirement of perturbed amplitudes is about 2 Gbytes; with 15 atoms, 30 electrons and 250 basis functions it rises to 5.5 Gbytes.

derivatives can be obtained as a simple byproduct of a force constant calculation. In the symmetric approach, it would be necessary to solve for derivatives of the wavefunction parameters with respect to the electric field to obtain them.

Analytic second derivatives at several levels of MBPT and CC theory have been implemented using the asymmetric strategy in the last 4 years. The required extension and generalization to force constant calculations of the original computer program for NMR chemical shifts at the CCSD(T) level was completed in 1997. Once this objective was achieved [57], it was straightforward to evaluate second derivatives at any order of MBPT up to MBPT(4) as well as CCD and CCSD and the approximate CC methods known as QCISD and QCISD(T) [50]. Extension to open-shell systems described by an unrestricted Hartree–Fock (UHF) reference determinant was reported the following year [58]. As alluded to above, the implementation is very general and can be used for any second-order property that corresponds to either real or imaginary perturbations. Calculations of any second-order property are relatively simple; the only requirement is that it might be necessary to program the integrals that correspond to the relevant perturbations.

2.2. *Implementation and practical considerations*

Because of differences among various orders of MBPT and levels of CC theory, it is rather difficult to give a description of computational aspects of the corresponding second-derivative methods that is both complete and concise. As a result, emphasis is placed on the CCSD and CCSD(T) methods in this section. For the most part, the most demanding computational steps in MBPT(3) and partial (without triples) MBPT(4) (SDQ–MBPT(4)) calculations are the same as those in CCSD, except that they are performed several times in the latter since the **T** amplitude equations are solved iteratively. CCD and QCISD can be viewed as approximations to CCSD in which some computationally inexpensive steps are omitted. In addition, the second derivative of the fourth-order triples excitation energy in MBPT(4) is evaluated in a similar way (but slightly lower cost) as that of the triple excitation correction that defines the CCSD(T). MBPT(2) is a special case to which the discussion below does not apply.

The general logical structure followed in our implementation of high-order MBPT and CC analytic second-derivative calculations is shown schematically in figure 1. After the unperturbed wavefunction and density have been constructed and stored, the corresponding perturbed quantities are evaluated and processed sequentially. The computationally dominant[8] procedures involved in analytic CCSD second-derivative calculations are as follows:

Step 1: solution of the set of coupled nonlinear equations that defines the **T** amplitudes;
Step 2: solution of the linear equation that defines the $\mathbf{\Lambda}$ amplitudes;
Step 3: construction of the two-particle density matrix, which involves contractions between **T** and $\mathbf{\Lambda}$ amplitudes;
Step 4: iterative solution of the linear equation that determines the $\partial\mathbf{T}/\partial\beta$ amplitudes;

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[8] The steps listed are those usually said to scale with the sixth power of the basis set. The scaling properties are actually dependent upon the number of occupied (n) and unoccupied (N) molecular orbitals, and the scaling will usually follow n^3N^3 or n^2N^4, depending on the ratio $N : n$.

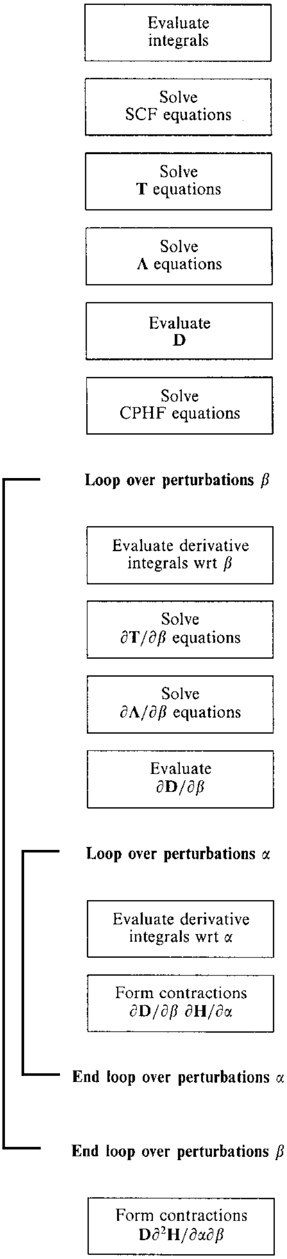

Figure 1. Flow diagram for CC analytic second-derivative calculations.

Step 5: iterative solution of the linear equation that determines the $\partial\mathbf{\Lambda}/\partial\beta$ amplitudes;

Step 6: construction of the perturbed two-particle density matrix, which consists entirely of $\mathbf{T}\partial\mathbf{\Lambda}/\partial\beta$ and $\mathbf{\Lambda}\partial\mathbf{T}/\partial\beta$ contractions.

Steps 1–3 are also required in analytic gradient calculations; the remaining three steps, steps 4–6 (which must be performed for all perturbations β), correspond to evaluation of differentiated counterparts of the terms evaluated in steps 1–3.

When very large basis sets are used, the number of unoccupied molecular orbitals is much greater than the number occupied orbitals; in this limit, the total number of arithmetic operations required in each iteration of steps 1, 2, 4 and 5 are approximately the same[9]. With smaller basis sets, the costs of steps 2 and 5 are still about the same, but determining **T** (step 1) is slightly more expensive than step 4. The number of operations needed to evaluate the first derivative of the density matrix is about twice that involved in calculating **D** itself. However, evaluation of **D** and $\partial \mathbf{D}/\partial\chi$ is non-iterative and steps 3 and 6 consequently require less time than the other four steps. In general, the time required to evaluate **D** and $\partial \mathbf{D}/\partial\chi$ is comparable with that for two or four iterations respectively of the unperturbed CCSD equations. Hence, the ratio of timings for steps 4–6 to those for steps 1–3 will be somewhat greater than unity. In addition, steps 4 and 5 require the (non-iterative) calculation of inhomogeneous terms that themselves have the cost of one iteration. Therefore, if translational and rotational invariance conditions are ignored and $3N$ nuclear displacement perturbations are considered explicitly[10], the cost of an analytic CCSD second-derivative calculation will usually be in the range (3–5) NZ, where Z is the cost of a single gradient calculation. In MBPT(3) and SDQ–MBPT(4), *each* of steps 4–6 is about twice as expensive as evaluation of the corresponding unperturbed quantities. Hence, the cost of analytic second-derivative evaluation for these methods is higher than for CCSD and should be close to $6NZ$.

Different considerations apply to CCSD(T). In this approach, non-iterative corrections due to triple excitations are evaluated, and the cost of these corrections is typically much greater than those which depend solely on single and double excitation amplitudes[11]. The most costly steps for CCSD(T) analytic second derivatives are listed below, with the first three again being required for gradient calculations:

Step 7: calculation of the unperturbed $\mathbf{T}_3$ amplitudes;
Step 8: calculation of triple excitation contributions to the $\boldsymbol{\Lambda}$ equations;
Step 9: calculation of contributions to the two-particle density matrix that involve the $\mathbf{T}_3$ amplitudes;
Step 10: calculation of the $\partial \mathbf{T}_3/\partial\chi$ amplitudes corresponding to perturbation χ;
Step 11: calculation of triple excitation contributions to the $\partial \boldsymbol{\Lambda}/\partial\chi$ equations;
Step 12: evaluation of triple excitation contributions to the perturbed one- and two-particle density matrices.

A more detailed discussion than given above for CCSD is warranted here so that the more complicated considerations that apply to CCSD(T) second derivative calculations can be made clear. To calculate the $\mathbf{T}_3$ amplitudes, two distinct contractions between double excitation **T** amplitudes ($\mathbf{T}_2$) and two-electron integrals are performed. To calculate the perturbed triple excitation amplitudes (step 10),

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[9] There is a single contraction with an n^2N^4 dependence that is required in each iteration for all these steps.

[10] It is trivial to exploit translational invariance, and our codes do this in both numerical and analytic force constant calculations. However, the discussion in this section is simplified if all $3N$ modes are considered.

[11] Contractions with n^3N^4 and n^4N^3 computational dependence are required in CCSD(T) and full MBPT(4) calculations.

five contractions are required. Two of these involve $\partial \mathbf{T}_2/\partial\chi$ amplitudes and unperturbed integrals while two of the others are similar but involve $\mathbf{T}_2$ and differentiated integrals[12]. Step 5 involves contractions between the unperturbed $\mathbf{T}_3$ amplitudes and the derivative Fock matrix and has a cost that is slightly less than the other four steps[13]. The costs of step 8 is comparable with that of step 7, and is about half that associated with step 11. The contributions of $\mathbf{T}_3$ to the unperturbed density matrix involve two additional contractions that again have roughly the same computational cost as steps 7 and 8. Step 12 requires contributions from $\mathbf{T}_3\partial\mathbf{\Lambda}_2/\partial\chi$ contractions as well as those between $\partial\mathbf{T}_3/\partial\chi\mathbf{\Lambda}_2$, and an additional contribution between $\mathbf{T}_3$ and $\partial\mathbf{T}_3/\partial\chi$ (which can again be avoided but at the cost of potential numerical instabilities); the overall cost is perhaps 2.5 times that of step 9. If disk storage was not an issue, the ratio of triple excitation contributions in second derivative and gradient calculations could be estimated as roughly 7–8:3. However, it is not practical to store the unperturbed triple amplitudes. In a general-purpose implementation, they must be recalculated within the outer loop over perturbation β (see figure 1). The overall cost ratio is therefore increased; a ratio of 3:1 represents a plausible and somewhat conservative estimate. In the limit that the computational time is completely dominated by the triples contribution, the cost of a CCSD(T) second-derivative calculation is expected to be about $9NZ_{\mathrm{T}}$ for a molecule with no symmetry and $3N$ nuclear displacement coordinates. Hence, relative to the cost of a gradient calculation at the same level of theory, CCSD(T) second derivatives are more than twice as expensive as CCSD. However, it should be stressed that this is an upper limit that is reached only in very large calculations.

A comparison of the costs of analytic force constant calculations with those associated with numerical differentiation of analytic first derivatives is appropriate at this point. Using double-sided numerical differentiation and ignoring translational and rotational invariance (these conditions are not an important consideration for large molecules, anyway), $6N$ gradient evaluations are needed; so the overall cost of the calculation becomes $6NZ$. Analytic evaluation of CCSD second derivatives is clearly the preferred choice; it is faster ((3–5) NZ) and requires only about twice the disk storage requirements of a gradient calculation. For MBPT(3) and SDQ–MBPT(4), the costs are comparable and the superior accuracy of the analytic procedure suggests that it should be favoured. However, if triple excitation effects account for more than about half of the overall computational cost for this example, it becomes more expensive to perform an analytic calculation than to use a finite-difference approach based on the force method. Therefore, one might question the wisdom of performing analytic force constant calculations at the CCSD(T) level of

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[12] The alert reader might wonder why a factor of two does not also apply to the calculation of the perturbed single and double $\mathbf{T}$ and $\mathbf{\Lambda}$ amplitudes (steps 4 and 5) at the CCSD level. Again, there are two classes of contractions involved in these calculations, $\mathbf{T}\ \partial\mathbf{H}/\partial\chi$ and $\partial\mathbf{T}/\partial\chi\ \mathbf{H}$. However, the former is constant throughout the iterative process and is evaluated once and stored on disk. This also provides the explanation for the qualitative differences between high-order MBPT and CCSD with regard to the cost of these steps.

[13] In principle, this step can be avoided in most cases. There are two such contributions, one involving the occupied–occupied block of the Fock operator and the other the virtual–virtual part. The former is partly avoided in our implementation by a special procedure (use of canonical perturbed occupied orbitals) that is discussed in [55], but the analogous treatment of the virtual–virtual contributions has not been implemented since it is likely to lead to numerical instabilities for very large calculations.

theory. While the approximate cost of triples in these calculations could be reduced to about $7NZ_T$ by storing the unperturbed $\mathbf{T}_3$ amplitudes, this is not a practical alternative for large molecules.

The analysis above ignores all issues associated with molecular symmetry. However, the vast majority of molecules studied by high-level quantum-chemical methods have at least one non-trivial element of symmetry[14]. For these, some of the gradients in the finite-difference procedure must be evaluated for displaced structures in which symmetry elements have been lost. On the other hand, the fully analytic procedure exploits the symmetry of the undistorted geometry at all points in the calculation. The treatment of symmetry in our code is restricted to the highest-order Abelian subgroup of the full molecular point group. In the most favourable case, the basis functions are partitioned equally among all irreducible representations, and it can be shown that the cost of calculation will scale inversely with the square of the order of the point group (h) [59]. In practice, however, the distribution of functions is usually not uniform and a somewhat lower factor is actually observed that is typically in the range (0.6–0.8) h^2. Even an optimal choice of distorted geometries in the finite-difference procedure requires that some of the calculations be carried out for point groups of order $h/2$. These gradient calculations are (roughly) a factor of three slower than those performed at the reference geometry or for totally symmetric displacements. As two extreme examples, consider the planar molecule HFCO and diborane. The HFCO molecule has C_s symmetry, and its Cartesian degrees of freedom can be resolved into eight totally symmetric displacements and four asymmetric displacements. To calculate second derivatives in a finite-difference procedure, 16 gradients must be evaluated in C_s symmetry and four in C_1 symmetry[15]. Therefore, the cost of calculating triple excitation contributions for the first class of gradients is $16Z_T$ and that of the second class roughly $12Z_T$. While considerably less favourable than at the CCSD level ($16Z$ for analytic versus $28Z$ for finite difference), the overall $28Z_T$ cost of the triple excitation contributions in the finite-difference procedure is about 80% of the $36Z_T$ expected in an analytic CCSD(T) calculation. For diborane, there are four totally symmetric and 20 asymmetric displacements. In this case, the expected triple excitation costs associated with finite-difference and fully analytic procedures are $68Z_T$ and $72Z_T$ (a factor of three rather than the value of four corresponding to the fully optimal exploitation of symmetry has again been assumed for the former); so the fully analytic procedure is expected to be about the same in this case. For pyridine (a C_{2v} molecule), the corresponding analytic and finite-difference costs are again expected to be about the same. Given the assumption that the cost associated with calculating the gradient at displaced points with lower symmetry is three times greater than at the unperturbed geometry, it is relatively straightforward to show that the total costs of triple excitation effects (in units of Z_T) for analytic and finite-difference force constant calculations are about $3n_T$ and $3n_T - n_S$ respectively, where n_S and n_A are the number of totally symmetric and asymmetric displacements and $n_T = n_S + n_A$. Hence, the fully analytic procedure is

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[14] All symmetry operations apart from the identity are regarded as 'non-trivial' in this context.

[15] Note that double-sided differentiation is used only for the totally symmetric displacements. For asymmetric displacements that transform as irreducible representations of Abelian point groups, positive and negative directions are equivalent by symmetry and only one gradient calculation is necessary.

most efficient when the ratio of asymmetric to symmetric modes is largest, but the finite-difference procedure should always be slightly faster given the present set of assumptions. In general, there is an advantage of approximately 25–50% associated with the finite-difference procedure when no symmetry is present; any symmetry at all makes them more competitive in cost.

The discussion above is based on a number of assumptions and idealizations and is intended only to give a general impression of the relative costs involved in these calculations. Timings are documented in table 2 for SDQ–MBPT(4), CCSD and CCSD(T) analytic and finite-difference harmonic frequency calculations for a number of molecules with varying amounts of symmetry, together with the corresponding ratios (the central processing unit time for the finite-difference calculation divided by that for the analytic). The algorithm used in the finite-difference calculations is designed to take maximal advantage of symmetry. Unlike most program packages that use individual atomic displacements, the procedure used here is based on symmetry-adapted displacements. This ensures that the order of the Abelian subgroup for all displaced geometries is at least half that corresponding to the undistorted molecule.

Overall, it can be seen that the rough estimates given above for SDQ–MBPT(4) and CCSD calculations are reasonably accurate in most cases. The analytic procedure is most advantageous at the CCSD level, where the timing ratios range from 1.37 (HOOF and N_2H_2) to 1.71 (HFCO). It should be noted that no dramatic increase in the timing ratio is found as the order of the point group increases. This is a consequence of the finite-difference algorithm since all calculations are run in either the full point group or a point group in which the order is half that of the undistorted structure. If an algorithm based on isolated Cartesian displacements of the atoms is used, then most gradient calculations would be run in C_1 symmetry. In that case, the timing ratio for a molecule such as diborane would be significantly greater than HFCO or HOOH, which is not observed here. The order of the point group for the unperturbed molecule is not an issue; the two factors that determine the overall ratio are the number of points run in full symmetry versus the number run in a lower-order point group as well as the relative cost of gradient calculations in the high- and low-symmetry point groups. The first criterion implies that timing ratios become more favourable as the number of asymmetric displacements increases relative to symmetric displacements, while the second criterion controls the numerical magnitude of the increase. If only the first criterion was operative, high-symmetry molecules such as diborane would have larger ratios in all cases than lower-symmetry structures. However, it turns out that the partitioning of orbitals among irreducible representations is less balanced in B_2H_6 than in the lower-symmetry HFCO and HOOH molecules, with the result that the analytic procedure is relatively faster for both of the latter. It should also be noted that the H_2CO and N_2H_2 examples given in table 2 provide something of a worst-case scenario for molecules belonging to point groups of order four; more than 60% of the displaced points are run in the full point group symmetry for both molecules. The documented timings for the CCSD(T) calculations superficially appear to be more favourable than a quick perusal of the discussion above might lead one to expect. However, this is simply because the time spent evaluating triple excitation effects does not overwhelm that associated with the CCSD calculation in any of the cases presented here. Some idea of the relative cost of the triples part of the calculation can be obtained by subtracting CCSD from CCSD(T) timings. For example, the

Table 2. Computational timings[a] for analytic and finite-difference calculations of harmonic force fields. All timings were obtained on a Compaq XP-1000 workstation running version Compaq Tru64Unix version 4.0F with version 4.2.1 of Digital Fortran.

			SDQ–MBPT(4)			CCSD			CCSD(T)		
Molecule	Number of functions	Symmetry	Finite-difference (s)	Analytic (s)	Ratio	Finite-difference (s)	Analytic (s)	Ratio	Finite-difference (s)	Analytic (s)	Ratio
HOOF	50	C_1	591	630	0.94	2749	2011	1.37	4155	4206	0.99
HOOH	66	C_2	749	543	1.38	2001	1222	1.64	2846	2260	1.26
HFCO	50	C_s	233	185	1.26	973	568	1.71	1468	1393	1.05
H_2CO	66	C_{2v}	228	172	1.33	566	350	1.62	780	632	1.23
N_2H_2	66	C_{2h}	178	166	1.07	493	361	1.37	712	639	1.11
B_2H_6	102	D_{2h}	1331	940	1.42	2512	1553	1.62	3558	2873	1.24

[a] Timings exclude contributions from integral evaluation.

time associated with calculating triple excitation effects for HOOF is 1406 s in the finite-difference procedure and 2195 s in the analytic procedure. The timing ratio is about 0.67, which is in the expected range for a molecule with no symmetry. To conclude this discussion, it should also be pointed out that the maximum disk storage requirement is approximately the same in the analytic and finite-difference approaches.

One additional and important feature of our implementation should be mentioned. While the most computationally efficient strategy for analytic MBPT and/or CC gradient evaluation requires both the unperturbed Hamiltonian and the two-particle density matrix to be simultaneously available, the corresponding perturbed quantities are also needed in analytic second-derivative calculations. Although it is convenient to have all these quantities available in the molecular orbital (MO) basis, their storage can become impossible in large-scale analytic second-derivative calculations where the integrals, derivative integrals with respect to β, $\mathbf{D}$ and $\partial\mathbf{D}/\partial\beta$ are all needed. The principal problem involves the quantities that are labelled by four virtual (unoccupied) orbital indices, as the number of these far outnumbers the rest when large basis sets are used. Fortunately, all terms that involve the four virtual index (FVI) integrals are easily formulated and evaluated in the atomic orbital (AO) basis [60, 61], and the same technique can be used for the derivative integrals provided that a symmetry-adapted AO basis is used. Hence, the formation of these quantities can be skipped in integral transformations and no disk space need be set aside for them. Such an option is available for the FVI integrals in our program for energy and gradient calculations, and for both unperturbed and differentiated FVI integrals in analytic second-derivative calculations. It is again convenient to store the FVI component of the two-particle density matrix, because the evaluation of orbital relaxation effects involves the calculation of certain intermediates that involve contractions between the density matrix and integrals. However, storage is unnecessary since the density matrix elements are themselves functions of the (easily stored) $\mathbf{T}$ and $\boldsymbol{\Lambda}$ amplitudes. Indeed, the two-particle density is truly needed only when contracted with differentiated integrals and it could in principle be calculated and processed 'on the fly'. However, that is one level of program optimization beyond our current implementation, in which both FVI perturbed and unperturbed density matrices are calculated and stored just before they are needed to contract with integrals. At these times, there are no other FVI quantities on disk. This AO-based procedure permits calculations with approximately 150–250 functions to be performed on workstations equipped with 5–10 Gbyte of disk space. While the MO-based procedure is certainly somewhat faster, the difference is only about 25% for calculations that do not involve triple excitation effects. For MBPT(4) and CCSD(T), the overall costs of the two procedures are closer since no FVI quantities contribute to the triples energy or its derivatives.

3. Applications

In this section, selected applications of our implementation of analytic second derivatives at high-order MBPT and CC levels are reviewed. While these approaches have been used to study a number of chemical and spectroscopic problems, the focus in this section is on those that have involved the calculation of anharmonic force constants.

The potential energy of a polyatomic molecule is conveniently represented by an expansion in dimensionless normal coordinates q [62]:

$$\frac{V}{hc} = \frac{1}{2}\sum_{i}\omega_i + \frac{1}{6}\sum_{ijk}\phi_{ijk}q_iq_jq_k + \frac{1}{24}\sum_{ijkl}\phi_{ijkl}q_iq_jq_kq_l, \tag{4}$$

where ω_i is the harmonic frequency in reciprocal centimetres and the q_i are scaled versions of the usual normal coordinates Q_i:

$$q_i = \left(\frac{2\pi c\omega_i}{\hbar}\right)^{1/2} Q_i. \tag{5}$$

For polyatomic molecules, the harmonic frequencies are usually not precisely known from experiment, and information about the cubic and quartic force constants (ϕ_{ijk} and ϕ_{ijkl} respectively) is even more scarce.

Values of harmonic and anharmonic force constants can be interesting in their own right. For example, the cubic force constant ϕ_{ijj} provides a quantitative measure of how the force constant for motion along the jth mode behaves as the molecule is distorted along q_i. However, the primary importance of cubic and quartic force constants in the present context is that they serve to connect fundamental properties traditionally calculated by quantum chemists (harmonic vibrational frequencies, moments of inertia and equilibrium bond lengths) to those more readily determined by experiment (fundamental vibrational frequencies, rotational constants and average bond lengths). The former type of calculation still constitutes the vast majority of those reported in the literature, but there is a decided trend towards accurate calculation of spectroscopic observables[16]. With the development of highly accurate treatments of electron correlation such as CCSD(T) and powerful computers that permit these methods to be combined with large basis sets, it is now possible to make very accurate predictions of spectroscopic observables. Alternatively, one can go in the opposite direction and apply corrections to spectroscopic data to determine fundamental molecular properties. The latter type of approach is the subject of section 3.1.

References will be made to several basis sets in sections 3.1 and 3.2. These include the following: a double-zeta plus polarization (DZP) set (2s1p for hydrogen; 4s2p1d for other atoms) that is based on a double-zeta set of Dunning [63] augmented by the polarization functions (p for hydrogen, and d for other atoms) of Redmon *et al.* [64]; a triple zeta plus double polarization set (TZ2P) set (3s2p; 5s3p2d) for oxygen, carbon and hydrogen that is fully described in [65]; the cc-pVXZ (X = T and Q, corresponding to (3s2p1d; 4s3p2d1f) and (4s3p2d1f; 5s4p3d2f1g), respectively) correlation-consistent series of Dunning [66] and the cc-pCVTZ and cc-pCVQZ basis sets (3s2p1d; 6s5p3d1f and 4s3p2d1f; 8s7p5d3f1g) [67], modified versions of the cc-pVTZ and cc-pVQZ sets that are believed to account properly for the correlation of core electrons. In addition, the cc-pVDZ basis augmented with diffuse functions (aug-cc-pVDZ) (3s2p; 4s3p2d) [68] is used. In the calculations summarized in this section, all electrons were included in the correlation treatment and spherical harmonic representations of d, f and g polarization functions were always used. A local version of the ACES II program system [69] was used in all computational studies reviewed here.

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[16] For a representative collection of studies, see the entire issues of *Spectrochimica Acta* A, 1998, **53** (8) and *Spectrochimica Acta* A, 1999, **55** (3).

3.1. *Determination of equilibrium geometries*

All isomers corresponding to a specific stoichiometry are defined by distinct minima on the potential energy surface. At these points, forces on the atoms vanish and the structure is said to be at its equilibrium geometry. Although it is recognized that this geometry provides the only unambiguous quantitative definition of molecular structure, precise equilibrium structures are known for relatively few polyatomic molecules. The principal reason for the dearth of information is that the equilibrium geometry is not related to any observable quantity in a direct way. Experiments are able to determine only some sort of average distance between nuclei [70]. For example, mean internuclear distances r_g corresponding to thermal distributions of vibrational states are usually measured by electron diffraction, while X-ray diffraction generally provides distances r_α between mean nuclear positions (which is not the same as r_g[17]). Molecular constants determined by rotational spectroscopy via fits to rovibrational Hamiltonians can be corrected (if the harmonic force field is known) to provide r_z distances, which are equivalent to the r_α separations in the vibrational ground state. Within second-order perturbation theory (anharmonicity is the perturbation here, and not electron correlation), it is possible to convert among any of these three measures of distance. It is also possible to derive the corresponding equilibrium structure from any of them if the quadratic and cubic force fields and temperature are known [71].

Rotational spectroscopy also provides other measures of molecular structure. Isotopic substitution is commonly used to establish so-called effective structures (r_0). These are usually obtained by least-squares adjustment of atomic coordinates to moments of inertia that are based on the assumption of a rigid molecular structure [72]. The effect that individual isotopic substitution has on measured rotational constants is used to define so-called substitution structures that are quantified by internuclear distances r_s [72]. While it can be shown that r_s lies half-way between r_e and r_0 for a diatomic molecule described by a Morse potential, it is not true for polyatomic systems where neither r_0 nor r_s has a precise geometrical interpretation.

Although ground-state rotational constants do not correspond directly to a physically meaningful set of internuclear distances, they can be related to those that are inversely proportional to the principal moments of inertia of the equilibrium structure using second-order perturbation theory [42, 73]. The equation that relates these constants (designated as B_e^γ for the γth inertial axis) to the corresponding ground-vibrational-state constants B_0^γ is usually written as

$$B_e^\gamma = B_0^\gamma + \frac{1}{2} \sum_i \alpha_i^\gamma, \tag{6}$$

where the α_i^γ are known as vibration–rotation interaction constants corresponding to normal mode q_i and the γth inertial axis. The α_i^γ depend on three contributions. Two of these are functions of the harmonic force field and account for effects of perpendicular vibrations on the internuclear distances (see the footnote at the beginning of this section) and the Coriolis interaction. The third depends explicitly on the cubic force constants ϕ_{ijj}, where i is restricted to totally symmetric coordinates q_i. More generally, it can be shown that each α_i^γ is proportional to the difference

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[17] An illustrative example is the oxygen–oxygen separation in CO_2. In the limit when all modes are harmonic, the r_α distance is precisely equal to twice the equilibrium CO separation, while the r_g distance is somewhat less because of the curvilinear nature of bending vibrations.

between the B^γ rotational constant in the state of the molecule in which mode i is excited and that in the ground vibrational state. In principle, these can be determined from high-resolution infrared and Raman spectroscopy, but complete sets of vibration–rotation interaction constants are available for only a few molecules. For polyatomics, determination is often complicated by Coriolis resonances (small denominators in the Coriolis contribution) which lead to a breakdown of second-order perturbation theory. However, as equation (6) clearly shows, the difference $B_e^\gamma - B_0^\gamma$ is not really a function of the individual vibration–rotation constants, but rather their sum. Since the B_0^γ constants are a property of the non-degenerate ground vibrational state, it follows that they should be entirely unaffected by resonances among vibrationally excited states. Indeed, the Coriolis contribution to the sum in equation (6) can be written in such a way that there are no troublesome denominators [43, 74]. While calculating the sum of the α_i^γ constants clearly poses no problem, experimental determination of the sum is possible only when all are known and free from resonances. When near-degeneracies are present, the individual contributions cannot be determined with any accuracy since the actual shifts in the rotational constants will differ appreciably from those predicted by second-order perturbation theory. It is sometimes stated in the literature that calculation of vibration–rotation constants is required to extract B_e^γ constants from experimental data. In addition to being technically incorrect, this notion also creates the misleading impression that an accurate determination of $B_e^\gamma - B_0^\gamma$ differences requires or implies (as the case may be) that the α_i^γ constants are themselves comparably accurate. The important point is that it is possible to determine B_e^γ constants reliably from experimentally measured B_0^γ values even when strong Coriolis resonances make the accurate calculation of α_i^γ constants impossible. Hence, the procedure discussed in this section can be applied to quite large molecules (provided that a sufficient number of isotopically substituted species have been studied) which are essentially never free of Coriolis resonances.

Once the harmonic and required ϕ_{ijj} force constants are calculated, equilibrium geometries can be determined by a straightforward procedure. First, the experimental rotational constants B_0^γ[18] are converted to what will henceforth be referred to as empirical B_e^γ values. When data are available for a sufficient number of isotopically substituted species (which are assumed to have identical equilibrium structures), the corresponding empirical r_e geometry is determined by least-squares adjustment of the atomic coordinates which best fits the empirical B_e^γ constants. For polyatomics, this mixed experimental–computational procedure seems to have first been used by Pulay *et al.* [75] in a study of methane using force constants obtained at the SCF level. The same procedure has been used together with quadratic and cubic constants calculated at the correlated level, most notably by Botschwina, Allen and their collaborators [43, 74, 76–78].

Calculations of cubic force fields are based on the following procedure.

(*a*) The molecular structure is optimized. The geometry is considered to be converged when all forces on the atoms are below about 10^{-7} au.

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[18] Usually, experimentally determined constants include some contribution from centrifugal distortion effects. In these cases, which include rotational constants fit to the *S* and *A*-reduced Hamiltonians and those that are a subset of what is known as Watson's determinable parameters, centrifugal corrections are calculated from the harmonic force field to convert the reported values into the corresponding B_0 constants. See [72] for details of the various Hamiltonians and centrifugal contributions.

(*b*) The harmonic force field is calculated and normal coordinates are determined.
(*c*) The cubic constants are evaluated by numerical differentiation of analytic second derivatives calculated at points that are displaced along the normal coordinates. For totally symmetric normal coordinates, double-sided numerical differentiation is used. When the set of isotopomers that will eventually be used in the least-squares fitting procedure includes structures with a lower point group symmetry than the unsubstituted species (e.g. the HDCO isotopomer of formaldehyde), then it is necessary to calculate all ϕ_{jkk} constants in which j corresponds totally symmetric modes in the common subgroup of all isotopomers. For displacements that correspond to asymmetric motion of the unsubstituted species, only one analytic second derivative calculation is needed.
(*d*) Empirical B_e^γ values are calculated for the unsubstituted isotopic species, using both centrifugal corrections and those from equation (6).
(*e*) The harmonic force field is calculated and the normal coordinates for the isotopically substituted species are determined.
(*f*) The ϕ_{jkk} constants are transformed to the normal coordinate representation of the other isotopomers. This is a linear transformation and requires that the ϕ_{jkk} constants corresponding to rotational modes k be included[19].
(*g*) Empirical B_e^γ values are calculated for the isotopically substituted species, using both centrifugal corrections and those from equation (6).
(*h*) Least-squares refinement of structural parameters is carried out to provide the best possible fit with the empirical B_e^γ constants.

Essentially all the computational time associated with this procedure occurs in (*a*)–(*c*) above, which have been completely automated with the required displacements automatically determined. The cubic force field calculation can be run in one of two modes. The first involves sequential evaluation of all second derivatives at displaced points and runs as a single job directed by a few input keywords. An alternative option is available in which input files for all displaced points are written out after the harmonic frequency calculation for the undisplaced structure. These can be run on several different machines simultaneously, with the result subsequently processed by a simple job script[20]. Using highly correlated MBPT and CC analytic second-derivative methods, cubic force fields and empirical equilibrium geometry determinations have been applied to several molecules in the past 2 years ranging in size from the ethynyl radical [79] to cyclopropane [80] and benzene [81].

The first equilibrium geometry study carried out with these techniques focused on the metastable dioxirane molecule, which is thought to play a role in the ozonolysis of ethylene [82, 83]. Dioxirane features a three-membered ring containing two oxygen atoms and a CH_2 group and is isoelectronic and isostructural with cyclic ozone. Determination of the structure of dioxirane (in particular the oxygen–oxygen separation) by quantum-chemical calculations has proven to be a very difficult problem. Values from correlated calculations reported in the literature are scattered over a considerable range [84]. For example, a CCSD(T) calculation with the TZ2P

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[19] Such force constants are non-zero because the system of normal coordinate is rectilinear [62]. While force constants for rotational modes vanish at the energy minimum, they are in general non-zero at displaced points, with the effect that ϕ_{jmm} (m is a rotation) are also non-zero.

[20] This is a particularly appealing realization of parallel processing!

Table 3. Equilibrium structures of dioxirane obtained by least-squares adjustment of atomic coordinates to B_e^γ values estimated from experimental rotational constants B'' and vibration–rotation effects calculated by theory. Estimated uncertainties for the CCSD(T)/cc-pVTZ level are given in parentheses.

Theoretical procedure	r_e(CO) (Å)	r_e(OO) (Å)	r_e(CH) (Å)	θ_e(HCH) (degrees)	Residual (MHz)
SDQ–MBPT(4)/DZP	1.3848	1.5141	1.0856	117.04	0.29
CCSD/DZP	1.3848	1.5138	1.0855	117.04	0.36
CCSD(T)/DZP	1.3845	1.5130	1.0856	117.05	0.59
SDQ–MBPT(4)/TZ2P	1.3845	1.5144	1.0855	116.97	0.44
CCSD/TZ2P	1.3846	1.5141	1.0855	116.97	0.51
CCSD(T)/cc–pVTZ	1.3846(7)	1.5133(3)	1.0853(23)	117.06(35)	0.25

basis set gives r_e = 1.547 Å while configuration interaction singles plus doubles (CISD) with a TZ2P basis augmented by f functions on carbon and oxygen and d functions on hydrogen yields a considerably shorter value of 1.465 Å. For the most part, however, the better calculations give r_e distances ranging from 1.51 to 1.55 Å. A low-temperature study by Suenram and Lovas [85] succeeded in recording the microwave spectrum of dioxirane, and studies of five different isotopomers permitted the substitution structure to be determined. The corresponding r_s oxygen–oxygen distance was found to be 1.516 Å, near the low end of the range of high-level quantum-chemical predictions.

In contrast with the wide range of r_e(OO) distances obtained by energy minimization, those based on empirical B_e^γ values determined at various levels of theory differ very little (table 3) [86]. With basis sets ranging in quality from DZP to cc-pVTZ together with the SDQ-MBPT(4), CCSD and CCSD(T) treatments of electron correlation, r_e distances range only from 1.5130 to 1.5144 Å. The distance corresponding to empirical B_e^γ constants obtained at the highest level of theory (CCSD(T) with the cc-pVTZ basis set) is 1.5133 Å, remarkably close to the r_s value. The largest element of the residual vector corresponding to differences between empirical B_e^γ values and those calculated from the inertia tensors for isotopomers at the refined structure exhibits a general downward trend as the level of theory is improved but is small (of the order of one part in 10^4) in all cases. Based on the analysis of these results, it was possible to establish that the equilibrium oxygen–oxygen distance in dioxirane is 1.5133 Å with an uncertainty of less than 0.001 Å. In order to obtain high accuracy for this troublesome parameter in an energy minimization procedure, it is evidently necessary to use CCSD(T) together with relatively large basis sets that include f and perhaps g functions on all non-hydrogen atoms; optimizations using the cc-pVQZ and cc-pVTZ basis sets give r_e(OO)= 1.5112 and 1.5136 Å respectively, while the TZ2P basis set (see above) gives a significantly longer distance.

Another illustrative example is propadienylidene (H_2CCC:), which has the distinction of being the smallest stable cumulene carbene. This molecule serves as a prototype for all larger H_2C_nC: species ($n > 2$). Like H_2CCC:, many of these molecules have been detected in the interstellar medium [87]. It is also thought that their electronic absorptions may account for some of the mysterious diffuse interstellar bands, the assignment of which is one of the longest-standing problems in astrophysics [88]. Accordingly, the fundamental properties of these molecules

Table 4. Empirical and optimized r_e structures of propadienylidene determined at various levels of theory. The numbering of the carbon atoms is the same as their coordination number.

	SDQ–MBPT(4)/ cc-pVTZ	CCSD/ cc-pVTZ	CCSD(T)/ cc-pVTZ	SDQ–MBPT(4)/ cc-pCVTZ	CCSD(T)/ cc-pCVTZ
			Obtained by fit to empirical B_e^γ constants		
$r(C_1C_2)$ (Å)	1.3278	1.3278	1.3277	1.3280	1.3280
$r(C_2C_3)$ (Å)	1.2862	1.2864	1.2864	1.2865	1.2869
r(CH) (Å)	1.0809	1.0814	1.0816	1.0817	1.0828
α(HCC) (degrees)	121.33	121.30	121.30	121.29	121.24
Maximum residual (MHz)	0.78	0.60	0.53	0.54	0.18
			Optimized values		
$r(C_1C_2)$ (Å)	1.3189	1.3184	1.3274	1.3312	1.3281
$r(C_2C_3)$ (Å)	1.2846	1.2846	1.2894	1.2918	1.2879
r(CH) (Å)	1.0791	1.0791	1.0812	1.0848	1.0837
α(HCC) (degrees)	121.34	121.30	121.30	121.30	121.27

are of great interest, and propadienylidene has been studied by electronic [89] and vibrational [90, 91] spectra in rare-gas matrices and microwave [92] as well as photodetachment [93] spectroscopy in the gas phase. An early empirical r_e structure determination for H_2CCC: was reported in the literature, but it turns out that the description of the CCC bending potential in this molecule requires very-high-level calculations and the published structure suffers systematic degradation because of this and a few other problems [92]. Table 4 shows empirical r_e structures determined with CCSD(T) and large basis sets as well as corresponding distances obtained by energy minimization [94]. While internuclear distances and angles eventually converge to essentially the same values, it is clear that the empirical parameters are already accurate to within 0.001–0.002 Å at the CCSD/cc-pVTZ level of theory while the minimum energy structure calculated at the same level is significantly inferior. In order to obtain a comparably accurate structure by energy minimization, it is apparently necessary to use CCSD(T) together with very large basis sets (the cc-pCVQZ set contains 312 basis functions). Again, the magnitude of the largest residual element associated with the empirical structures exhibits improvement as the quality of the methods used to determine the quadratic and cubic force fields is improved. This is comforting, in the sense that it suggests that the treatment of the vibration–rotation interaction by perturbation theory is appropriate and that the right answer is being obtained for the 'right reason'.

Estimates of the r_e structure of cyclopropane have previously been made in the literature. One of these was based on the use of a simple model of anharmonicity to correct average internuclear separations determined by electron diffraction [95] while the other used experimentally determined ground-state rotational constants and vibration–rotation interaction constants to deduce the three independent geometrical parameters [96] for this D_{3h} molecule. Both of these studies also deduced r_z structures by correcting experimental data for vibrational effects in the harmonic approximation. While r_z carbon–carbon distances from the two studies agree rather well (1.516 and 1.513 Å for the microwave and electron diffraction studies respectively), there is a significant discrepancy in the corresponding r_e distances (1.510 and 1.501 Å) where magnitudes of the anharmonic corrections differ by a factor of two. To resolve the discrepancy, an empirical r_e structure was determined using the SDQ–MBPT(4) treatment of correlation together with the cc-pVTZ basis set [80]. It is perhaps not surprising that a carbon–carbon distance intermediate between those based on the electron diffraction and microwave studies is obtained, revealing that anharmonic effects were slightly overestimated in the latter and underestimated in the former. Adjusting the observed rotational constants for effects of vibration-rotation interaction gives an empirical equilibrium carbon–carbon distance of 1.503 Å. This is just slightly greater than that based on the electron diffraction data and is supported by a large scale CCSD(T) geometry optimization carried out with the cc-pVQZ basis set (345 basis functions). That the problem with experimental determination is almost entirely associated with the characteristic lack of knowledge regarding anharmonic force fields is reflected in r_z distance calculated from the r_e value and the cubic force field. This value (1.5111 Å) is within the uncertainty ranges spanned by both experimental estimates of this quantity.

It is our belief that the combination of rotational constants determined by microwave spectroscopy and cubic force fields calculated with high-level quantum-chemical methods represents the most reliable and economical means for determining the equilibrium structure of molecules. When good experimental data exist for a sufficiently large number of isotopomers that the number of independent rotational constants exceeds the number of independent geometrical parameters, empirical equilibrium structures can always be obtained. The high-level MBPT and CC analytic second-derivative procedures offer a significant asset for studies of this sort since the calculation of cubic force constants can be carried out in a very efficient way for relatively large molecules. Cyclopropane is an excellent example, as a purely numerical evaluation of cubic force constants for a molecule of this size is not a feasible proposition.

3.2. *Calculation of fundamental vibrational frequencies*

When the procedure described in section 3.1 is used to calculate the entire cubic force field, sufficient data are generated to evaluate all quartic force constants of the form ϕ_{iijk} by numerical second differentiation, that is

$$\phi_{iijk} = \frac{\phi^{+}_{jk} + \phi^{-}_{jk} - 2\phi_{jk}}{\Delta^2}, \tag{7}$$

where ϕ^{+}_{jk} and ϕ^{-}_{jk} are force constants evaluated analytically at positive and negative values of displacements (which may be equivalent by symmetry) of magnitude Δ along normal mode q_i. This is an especially convenient subset of quartic force constants, since only the diagonal and semidiagonal quartic constants (ϕ_{iiii} and ϕ_{iijj} respectively) appear in the expressions for vibrational energy levels that are derived from second-order spectroscopic perturbation theory [42]. Hence, when the cubic force field is determined with the approach described in the preceding section, all information needed to estimate the positions of fundamental, overtone and combination vibrational transitions of the molecule is obtained as a simple by-product of the calculation. The advantages of using normal coordinate displacements, plainly evident in the present context, were first pointed out by Schneider and Thiel [97]. Thiel and co-workers have applied this procedure using analytic second derivatives at the MBPT(2) level to a number of molecules [98] including difluorovinylidene [99] (which is related to the vinylidene molecule discussed later in this section) and most recently with CCSD(T) using our analytic second-derivative implementation [100]. Provided that one is interested only in the vibrational frequencies of a specific isotopomer, the approach outlined here is extremely efficient. Since the ϕ_{ijkl} constants are not needed, the number of displaced points used in the analytic second-derivative calculations scales only linearly with the number of atoms in the system. Hence, the overall cost of the calculation exhibits a cost that scales quadratically. The alternative approach of evaluating the entire quartic force field (in any coordinate system, as the corresponding force constants can be subsequently transformed to the normal coordinate representation) is significantly more expensive, scaling with the third power of the molecular size when analytic derivative methods are used and the fourth power when all force constants are determined from numerical differentiation of calculated energies. However, it should be mentioned that the study of quantum-dynamical phenomena such as intermolecular vibrational relaxation requires the full force field and the latter type of calculation is needed in such cases. In addition, when all quartic force constants are known for the normal isotopomer, those for any isotopically substituted species can be obtained by linear transformation in the same way that cubic constants for isotopomers are obtained in empirical r_e structure determinations.

Before continuing, it should be mentioned that the work of Lee, Taylor and Martin (see [40, 41] and references therein) in the area of highly accurate force field and frequency calculations at the CCSD(T) level pre-dates our recent efforts in this area and has dealt with a wide scope of examples. For the most part, their work has focused on molecules containing three to five atoms with all force constants determined solely from energy calculations, and their very careful and detailed analysis of available experimental data has shown that the CCSD(T) method combined with very large basis sets provides offers an extremely accurate representation of molecular force fields. It can fairly be said that their calculations have provided a majority of the highly accurate anharmonic force fields that are known for molecules of this size.

In the calculation of vibrational energy levels for polyatomic molecules using spectroscopic perturbation theory, Fermi resonances (small denominators) are a relatively common occurrence. Unlike the easily avoided issue of Coriolis resonance in empirical structure determinations, a proper determination of the affected energy levels must deal explicitly with the quasidegeneracy. The usual procedure is to treat all off-diagonal coupling in the vibrational Hamiltonian (which is expressed in a multidimensional harmonic oscillator basis) by perturbation theory except the blocks that couple the quasidegenerate level. The corresponding diagonal elements are modified and then the energy levels are obtained by diagonalizing the projection of the resulting effective Hamiltonian in the basis of interacting states [42]. This is not entirely satisfactory, as it is not clear where one should draw the line between interactions that are treated solely by perturbation theory and those that require the most comprehensive diagonalization. Denominator arguments alone are not completely sufficient because very large anharmonic force constants coupled with what might appear to be 'safe' denominators can lead to poor performance of perturbation theory. In other cases, where experimental analysis is very complete and detailed, deperturbed vibrational frequencies are determined and reported. These correspond to calculated values that assume vanishing off-diagonal elements in the projection of the effective Hamiltonian and are easily calculated by simply skipping the diagonalization step. However, when one is interested in the prediction of vibrational spectra rather than the confirmation of detailed spectroscopic studies, only the first option is acceptable. Nevertheless, for the examples discussed below, a strong Fermi resonance occurs only for one of the modes of diborane, where a deperturbed value is available [101], while the fundamental modes of vinylidene and propadienylidene are free from these effects.

While it has long been appreciated that significant discrepancies exist between harmonic frequencies calculated for motions involving the four-membered ring in diborane and those obtained from the experimentally inferred harmonic field [102–104] of Duncan *et al.* [101], the source of the problem had not been identified until 2 years ago [105]. At various correlated levels ranging from MBPT(2) to CCSD(T), very poor agreement has consistently been reported for two of these modes. Calculated values for the b_{1g} and b_{3u} stretching modes (the latter as the strongest absorption in the infrared) are in the ranges 1910–2000 and 1750–1820 cm^{-1} respectively, which are both 100–200 cm^{-1} higher than those based on the inferred harmonic force field (1814 and 1652 cm^{-1}). Arguments based on valence bond resonance structures have been given in support of the idea that a multireference treatment is needed to provide an accurate description of the potential for these motions [104]. However, that would be most unexpected and surprising since a vast amount of experience has suggested that even low-order MBPT methods treat correlation effects in the boranes quite satisfactorily [106]. To address this question, we thought it best to perform calculations of the actual experimental observables, namely the fundamental frequencies, rather than to grind away with refining the methods used to calculate the harmonic force field in the hope that the harmonic frequencies would eventually come into agreement with the 'experimental' values. As clearly seen in figure 2, essentially all the apparent disagreement between theory and experiment is associated with inadequacies in the empirical harmonic force field of [101]. When fundamental frequencies are calculated by combining CCSD(T)/cc-pVTZ harmonic frequencies with anharmonic corrections obtained at the CCSD level with the same basis set, spectacular agreement is achieved with experiment for the b_{1g} and b_{3u} stretching modes. Differences of 2 and 4 cm^{-1} are found, with the other ring stretching modes in only slightly poorer agreement[21]. By far the largest discrepancy is found for a torsional mode where the calculated and observed values of 1091 and 1020 cm^{-1} differ by 71 cm^{-1}. It is interesting to note that while much attention had been given to the ring stretching modes in the literature, the apparently troublesome torsional mode escaped attention because calculated and empirical harmonic frequencies agree rather well.

A second example is provided by vinylidene (H_2CC:), which is the smallest cumulene carbenes. While this molecule has a subpicosecond lifetime because of facile rearrangement to acetylene via a 1, 2 hydrogen shift, it nonetheless has a celebrated history in physical chemistry. Vinylidene was first studied theoretically in [107], where initial debate focused on the question of whether the molecule was stable or rather the transition state for hydrogen scrambling in acetylene. Proof of its quasi-stable existence emerged in two classic experiments by Lineberger and co-workers [108] who observed H_2CC: as the final state in the photoelectron spectrum of the

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[21] The ring stretching modes are those at 2088, 1603, 1925 and 1760 cm^{-1}.

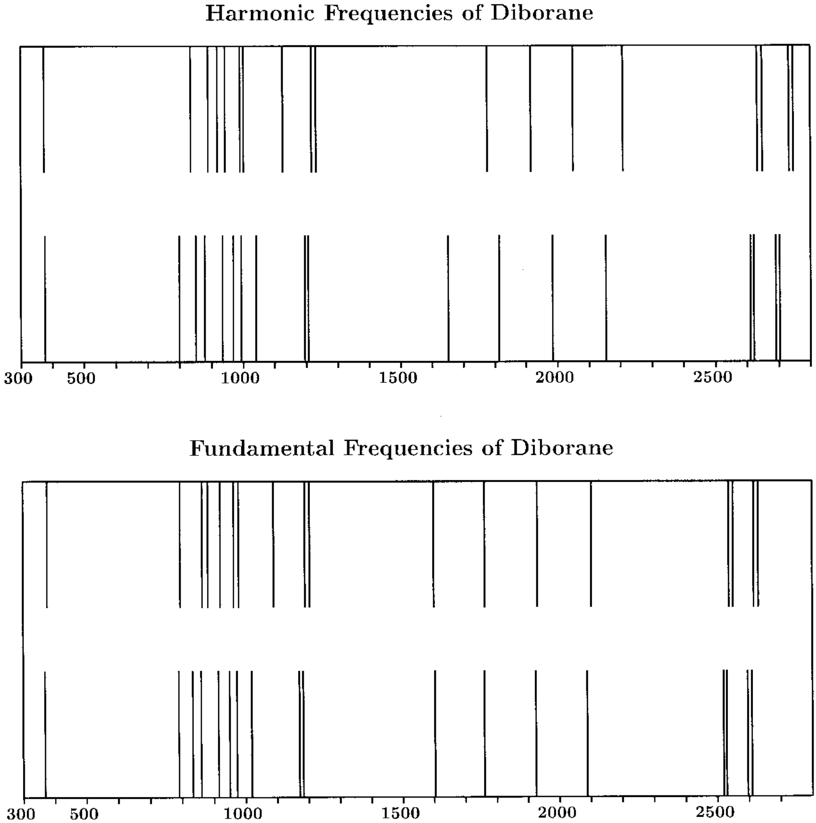

Figure 2. Positions of calculated (upper trace) and experimental (lower trace) vibrational frequencies of diborane. The 'experimental' harmonic frequencies are based on the empirical force field of [101]. See text for a description of the computational methods.

corresponding anion. Study of vibrational structure in the photodetachment spectrum revealed a wealth of information about the vibrational levels and isomerization dynamics of vinylidene [109]. One very curious observation was an extremely large anharmonicity associated with the HCH rocking mode, which serves as the initial reaction coordinate for the 1, 2 hydrogen shift. Harmonic frequencies calculated for this mode at various levels of theory lie near and sometimes above the $450 \pm 30\,\mathrm{cm}^{-1}$ band that was assigned to the first overtone of this mode [109]. The possibility that the assigned feature corresponds to the fundamental transition was discarded because it is not a totally symmetric vibration. Since the experiment gave no other indication that either the anion or the neutral does not have C_{2v} symmetry, the fundamental mode is expected to exhibit no Franck–Condon activity. As a result, it can only be concluded that the anharmonicity is so large that the harmonic approximation (which would place the transition several hundred wavenumbers above the observed position) is completely useless for describing this mode. Clearly, calculation of the vibrational energy levels of vinylidene is a challenging problem for theory which tests both the validity of the second-order treatment of anharmonicity and the quality of the calculated force field. Moreover, it is an important problem since

Table 5. Vibrational frequencies of propadienylidene calculated with CCSD(T). The harmonic frequencies are those obtained with the cc-pCVTZ basis set while anharmonic corrections $\nu_i - \omega_i$ were calculated with the cc-pVTZ basis.

	Harmonic frequency (cm^{-1})	Infrared intensity ($km\,mol^{-1}$)	Fundamental frequency (cm^{-1})	Experimental fundamental[a] (cm^{-1})
a_1 symmetry				
ν_1	3123	5	2997	3050–3060
ν_2	1998	250	1956	1952–1963
ν_3	1495	10	1458	1447–1449
ν_4	1119	2	1111	—
b_1 symmetry				
ν_5	217	3	211	—
b_2 symmetry				
ν_6	3212	0	3069	—
ν_7	1052	3	1034	—
ν_8	1020	19	996	999–1005
ν_9	275	114	287	—

[a] From [90].

the quality of results should give some indication of how similar calculations will fare for as-yet-unstudied substituted vinylidenes.

The position of the HCH rocking mode overtone transition is calculated to be 479 cm^{-1} using CCSD(T) and the cc-pCVTZ basis set [110]. This value is within the range spanned by the experimental uncertainty estimates and seems remarkably accurate when one considers how large a perturbation anharmonicity is in this case. While one might expect second-order perturbation theory to perform poorly, this is evidently not the case for the rocking potential. In addition, the calculated position of the $0\rightarrow4$ transition of this mode (767 cm^{-1}) is also in good agreement with a band at about 730 cm^{-1} tentatively assigned to this transition [109]. For the other vibrational energy levels, of course, anharmonic effects are less dramatic; the calculated energy levels are in excellent agreement with the experimental values in all cases. It therefore appears that calculations of the vibrational levels of substituted vinylidenes might prove valuable for assigning vibrational structure in the corresponding spectra. To support this point further, a simulated photoelectron spectrum of the vinylidene anion is shown in figure 3 together with the experimental data of Ervin, Ho and Lineberger. In the simulation, peak positions are located at the CCSD(T)/cc-pCVTZ fundamental, overtone and combination frequencies, while intensities are calculated in the Franck–Condon approximation with explicit treatment of Duschinsky mixing effects [111]. Franck–Condon factors are based on the CCSD(T)/aug-cc-pVDZ geometries and harmonic force fields of the neutral and anion, and each peak is represented by a Lorentzian with a full width at half maximum of 80 cm^{-1}. This plot rather dramatically illustrates that high-level calculation of structures and molecular force fields offers a valuable aid in assigning the spectra of unstable or unusual molecules.

The final molecule discussed in this section is the next largest cumulene carbene,

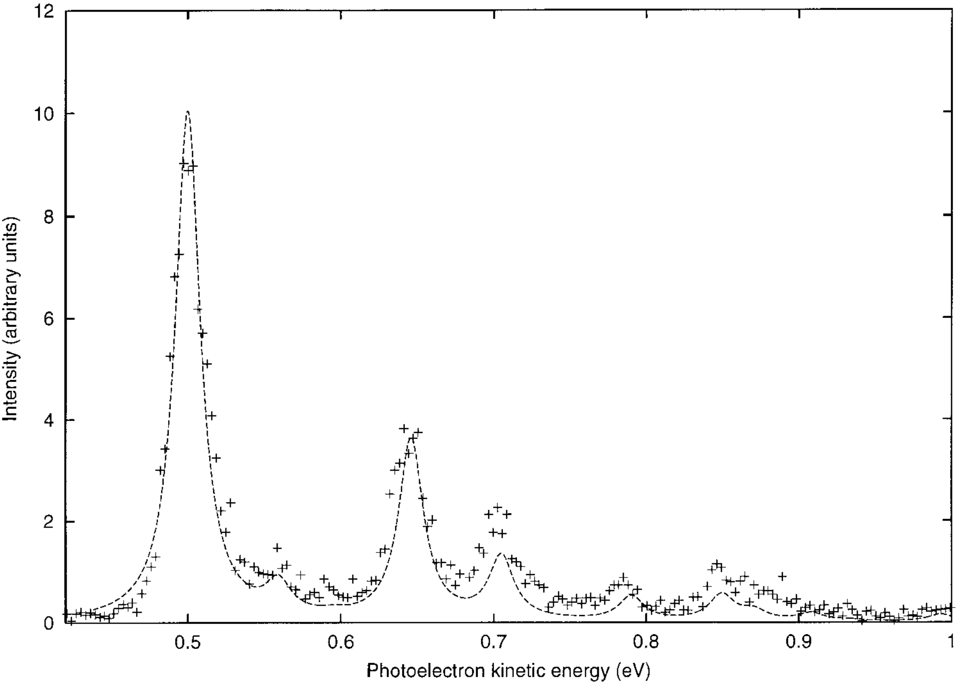

Figure 3. Observed (+) and simulated (- - -) photodetachment spectra of the vinylidene anion. The origin of the simulated spectrum is positioned so that it coincides with that of the experimental spectrum. A full description of the parameters used in the simulated spectrum is given in the text.

propadienylidene. This molecule, which was also discussed in section 3.1, has been studied in rare-gas matrices where both electronic [89] and vibrational [90] spectra have been recorded. Together, the electronic spectrum (which is well understood) and the infrared spectrum serve as markers for monitoring the presence and depletion of this species in photochemical experiments [91]. While its electronic and microwave spectra have been analysed with high-level CC methods, the vibrational spectrum has received somewhat less attention. This situation is remedied here. Table 5 lists fundamental frequencies calculated for this species along with values observed in an argon matrix and assigned by Maier *et al.* [90]. Two values are given for all but one of the latter since site effects split the corresponding absorptions into doublets. The calculated values are based on CCSD(T)/cc-pCVTZ calculations for the harmonic force field with anharmonic corrections obtained with CCSD(T) and the cc-pVTZ basis. For all but one of the transitions assigned by Maier *et al.*, the differences between calculated and observed frequencies is less than 10 cm^{-1}. However, an extremely large discrepancy is apparent for the totally symmetric CH stretching mode, where the calculated value of 2997 cm^{-1} is more than 50 cm^{-1} below the frequency of 3050–3060 cm^{-1} which was assigned to this mode. The experimental assignment was guided by relative intensities calculated for the ν_1 and ν_6 modes at the MBPT(2) level [90]. As in the calculations reported here, the former was predicted to have a much larger intensity than the latter, and the observed transition was therefore assigned to ν_1. However, we believe that the observed absorption can instead be confidently assigned to ν_6, which is predicted by theory to lie at 3069 cm^{-1}.

Indeed, it seems rather unlikely that the calculated values are more than 50 cm^{-1} in error. For acetylene, the same theoretical treatment gives 3369 and 3297 cm^{-1} for the antisymmetric and symmetric stretching modes [112], which differ only a little from the experimental values of 3373 and 3288 cm^{-1} [113].

Since analytic dipole moment derivatives are obtained for essentially no additional cost in a quadratic force constant calculation, they may also be differentiated numerically when cubic or quartic force fields are calculated in much the same way that the quadratic force constants are processed. This point is made because all coefficients a_i, a_{ij} and a_{ijj} in the dipole moment expansion

$$\mu = \mu_e + \sum_i a_i q_i + \tfrac{1}{2} a_{ij} q_i q_j + \tfrac{1}{6} a_{ijk} q_i q_j q_k + \cdots \tag{8}$$

can be obtained by these means, and only these are needed to obtain infrared intensities that are correct up to second order [114]. Generally, infrared intensities are calculated in the double-harmonic approximation in which the potential and dipole moment function are assumed to be quadratic and linear functions respectively of the coordinates. At this level of approximation, the intensities of overtone and combination bands vanish. The first-order correction contributes to overtone and combination intensities while the second-order correction makes a contribution to the intensities of fundamental transitions. Hence, the quadratic and selected cubic coefficients in the dipole moment expansion are a most convenient byproduct of quartic force field calculations that we have not yet exploited. Although it is quite likely that the refined estimates of fundamental transition intensities will have little impact in chemical applications (the residual error in the double harmonic approximation due to basis set and correlation error is probably at least as large in magnitude as the second-order correction), the ability to estimate which if any of the overtone and combination bands might appear prominently in the spectrum should be very useful. In passing, we note that, while the incremental cost of obtaining the dipole moment expansion coefficients is negligible in our approach, it represents a significant incremental cost when strictly numerical procedures are used.

4. Summary

The applications discussed in the previous section of this review are those that involve calculations of anharmonic force fields for polyatomic molecules. However, it should be emphasized that the high-order MBPT and CC analytic second derivative methods are also beneficial for other types of calculation. As demonstrated here, these calculations are usually faster for the calculation of harmonic frequencies and infrared intensities than those based on a finite-difference scheme. Hence, analytic second derivative methods are well suited to use in routine application studies, which typically involve the evaluation of these properties. A particularly interesting class of applications involves the study of open-shell systems that have so-called Hartree–Fock instabilities. In these cases, it is often not possible to obtain solutions to the SCF equations at distorted geometries of lower symmetry that correlate to solutions that transform as a pure irreducible representation of the point group at the undistorted geometry. It is accordingly very difficult to determine the harmonic force field for systems of this type. While it is often thought that the presence of an instability implies strong coupling of the pseudo-Jahn–Teller type and a consequent need for a multireference treatment, these problems often occur even in cases where there are no near-degeneracies in the actual spectrum. Calculations of the harmonic force field are of course straightforward when analytic procedures are used. Results obtained for two systems with UHF–CCSD(T) that had not previously been studied at this level of theory, namely the formyloxyl and nitrogen trioxide radicals, are in good agreement with high-level multireference approaches and experiment respectively and call into question the common wisdom that single-reference approaches are insufficient for problems of this type [115].

As stated earlier, our implementation of the asymmetric approach can be applied to evaluate any second-order property that corresponds to either real or formally imaginary perturbations. Perhaps most prominent among the latter type is the magnetic shielding tensor that governs NMR chemical shifts. In fact, this was the application area to which these methods were first applied. Several studies demonstrated that very accurate NMR chemical shifts can be obtained with CCSD(T). One particularly notable example is the cyclopropylcyclopropylidenemethyl cation, for which the chemical shift calculated for the carbocation centre with MBPT(2) differs from the experimental value by more than 20 ppm [116]. On the basis of this discrepancy, the extent to which the structure of this molecule is affected by solvation in superacid solution was called into question [117] despite the fact that these solutions are known to be non-coordinating. However, all doubt was removed when the NMR spectrum was calculated at the CCSD(T) level, where the calculated and measured NMR shifts are 234.1 and 234.2 ppm respectively [118]. Calculations of the magnetic resonance spectrum of this and other vinyl cations have been reviewed elsewhere [119]. In another application, CCSD(T) calculations were used to establish a reliable absolute scale for ^{17}O shieldings [120]. Quite recently, NMR chemical shift calculations at the CCSD(T) level played a vital role in the laboratory identification of the N_5^+ ion, the first all-nitrogen species to be synthesized in more than a century [121].

Additional second-order properties that have been calculated with analytic second derivative methods including triple excitation effects include indirect nuclear spin–spin coupling constants [122], spin rotation constants [123] and electric polarizabilities [124, 125]. Analytic second derivatives have also recently been implemented at the CCSDT-1, CCSDT-2, CCSDT-3 and CC3 levels of theory, all of which include an iterative treatment of triple excitations effects [126]. With the completion of that project, the roster of MBPT and CC methods for which analytic second derivatives are available has been expanded to all methods in table 2 that have either an N^6 or N^7 computational dependence and includes all methods for which analytic first derivatives are available. We have recently implemented third derivatives at the CCSD and CC3 levels [125] that do not include orbital relaxation effects. The Århus group has also implemented both third and fourth derivatives of the unrelaxed CCSD energy [127, 128]. In some respects, going from analytic first to second derivatives is a more difficult process than extending an analytic second-derivative implementation to third derivatives. The reason is again the $2n + 1$ rule; only the first derivatives of the wavefunction are required to evaluate third derivatives and these are already evaluated in an analytic second derivative calculation. While our implementation is currently restricted to one-electron perturbations (which yield hyperpolarizabilities when the electric field perturbation is chosen), extension to cubic force constant calculations would require that third derivatives of one- and two-electron integrals be calculated as well as the corresponding two-particle density matrix contributions, and these are not implemented in our programs. Finally, dynamical (frequency-dependent) properties can be calculated with a very simple generalization of an analytic derivative program and moreover cannot be evaluated by standard numerical differentiation techniques. Our codes have this capability and have been used to calculate frequency-dependent electric polarizabilities and hyperpolarizabilities [124, 125, 129, 130], again using unrelaxed orbitals. It must be emphasized that the calculations discussed immediately above (third derivatives and dynamical properties) are not simply for pilot-scale applications. Indeed, our codes have been used to calculate frequency-dependent hyperpolarizabilities for the water molecule using basis sets that contain more than 150 contracted Gaussian functions [129].

Levels of theory such as CCSD(T) include a nearly quantitative treatment of electron correlation for many molecules, and the availability of analytic second- and third-derivative methods for these methods opens up exciting possibilities for chemical applications. The computational requirements associated with these approaches are discussed in great detail in this review. For all properties such as quadratic force constants that can also be evaluated with finite-difference techniques, the corresponding analytic procedures are always comparable in cost or faster and do not have excessive disk storage requirements. For many other applications (NMR chemical shifts and other magnetic properties, force constant calculations for systems exhibiting Hartree–Fock instabilities and frequency-dependent properties), finite-difference procedures cannot be used and analytic procedures are the only viable option. The new millennium is truly an exciting time for quantum chemistry. A long-standing goal of the field has been to calculate molecular properties and spectroscopic observables with near-quantitative accuracy. While success was achieved long ago in this pursuit for diatomic and triatomic molecules, similar levels of accuracy have been achieved for larger systems only in recent years. As demonstrated by the applications presented in the previous section, the use of analytic second-derivative procedures at high levels of theory such as CCSD(T) represents an important advance towards this objective.

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