Geometry optimization using improved virtual orbitals: A complete active space numerical gradient approach

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The improved virtual orbital-complete active space configuration interaction (IVO-CASCI) method is extended to enable geometry optimization and the calculation of vibrational frequencies for ground and *excited* states using numerical energy gradients. Applications consider the ground state geometries and vibrational frequencies of the Be_2, LiF, H_2S, and HCN molecules, as well as excited state properties for HCN, systems that are sufficiently complex to access the efficacy of the method. Comparisons with other standard approaches (self-consistent field, second order Möller-Plesset perturbation theory, complete active space self-consistent field, and coupled cluster singles and doubles methods) demonstrate that the numerical gradient version of the IVO-CASCI approach generally fares comparable to or better for all systems studied. The accurate estimates for the Be_2 bond length and vibrational frequency are notable since many other computationally facile methods produce poor results. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2566692]

I. INTRODUCTION

Molecular geometries and vibrational frequencies are essential ingredients in finding the reaction paths and in identifying the end products of a chemical reaction. The theoretical determination of optimized molecular geometries and vibrational frequencies requires the computation of derivatives of the total energy with respect to all internal coordinates, something which becomes a daunting task for excited states, highly open-shell systems, and transition states where multiconfigurational treatments are necessary to describe the important contributions from nondynamical electron correlation.

Ideally, energy gradient should be determined analytically. However, the analytic evaluation of energy gradients requires the direct computation of the derivatives of molecular orbitals and of the expansion coefficients in the configuration interaction (CI) wave function with respect to all nuclear degrees of freedom. Considerable effort has enabled evaluation of these derivatives for various self-consistent field (SCF), CI, and single reference configuration second order Möller-Plesset perturbation theory (MP2) methods.[1–5] Typically, energy gradient calculations are performed for the ground electronic state, but these gradient calculations can, in principle, be accomplished for excited states as well. However, methods have been lacking for the evaluation of analytic energy gradients for multireference perturbation theory (MRPT) methods because of the complexity of the MRPT methods.

As a potential avenue for including these nondynamical contributions to energy gradients, we have previously presented the general theory for the evaluation of analytical energy derivatives[6] for the effective valence shell Hamiltonian (H^v) (Ref. 7) method, a complete active space (CAS) MRPT approach of the "perturb then diagonalize" variety that has been demonstrated to generate highly accurate, correlated *ab initio* predictions for electronically excited states and their global potential energy surfaces.[8] This *ab initio* energy derivative formulation of MRPT is facilitated by special features of the H^v method. The use of CAS implies that H^v computations proceed by diagonalizing an effective valence shell Hamiltonian H^v, and therefore the analytical derivative may be represented through the Hellmann-Feynman theorem[9] in terms of analytical derivatives of H^v.

While the theory for analytical energy gradients is available,[6] we apply the "improved virtual orbital-complete active space CI" (IVO-CASCI) geometry optimization method here using numerical derivatives in order to test the accuracy before coding the much more complicated analytical derivative routines. Thus, the present work provides the first application of energy gradients to the problem of geometry optimization and the computation of vibrational frequencies for both ground and excited electronic states using the IVO-CASCI approach, which is the first order approximation within the H^v method.

The IVO-CASCI scheme is computationally simpler than the CI-singles (CIS) and complete active space SCF (CASSCF) methods. The latter arises because the IVO-CASCI method does not require iterations beyond those in the initial SCF calculation, nor does it possess features that create convergence difficulties with increasing size of the CAS in CASSCF calculations. Since the IVO-CASCI approach contains both singly and doubly excited configurations in the CAS (in addition to higher order excitations), it

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provides descriptions of both singly and doubly excited states with comparable accuracy to CASSCF treatments.[10] The latter contrasts with the CIS method which cannot treat doubly excited states.

The IVO-CASCI scheme differs from the traditional CI and MP2 approaches in the evaluation of orbitals and orbital energies. The traditional CI and MP2 methods determine both the occupied and unoccupied orbitals and their orbital energies using a single Fock operator in which the unoccupied orbitals describe the motion of an electron in the field of N other electrons. Consequently, the virtual orbitals are, at best, more appropriate for describing negative ion states than the low lying excited states of interest. The IVO-CASCI method obtains the unoccupied orbitals and their energies from a set of V^{N-1} potential Fock operators in order to optimize the CASCI predictions of low lying electronic states and thereby to minimize the higher order perturbative corrections. The generation of the improved virtual orbitals resembles the approach proposed long ago by Silverstone and Yin[11] and Huzinaga and Arnau[12] which is a special case of the extended Hartree-Fock method of Morokuma and Iwata.[13]

The IVO-CASCI method has been demonstrated to be accurate for calculating atomic spectra,[14,15] diatomic potential energy curves,[16] and the electronic spectra of complex molecular systems[17,18] such as porphin. The method has also been adopted in multireference Möller-Plesset studies by Choe *et al.*[19] Here, we extend the IVO-CASCI approach to enable the determination of optimized ground state (and some excited state) geometries and vibrational frequencies using numerical energy gradients. Applications are provided to the Be_2, LiF, H_2S, and HCN molecules, systems which are sufficiently complex to access the efficacy of our method. The computed geometries and vibrational frequencies are compared with those obtained from SCF, CASSCF, MP2, and coupled cluster with singles and doubles excitations[20] (CCSD) methods. The IVO-CASCI method is one portion of the latest generation of effective valence shell Hamiltonian computer codes that have been interfaced to the GAMESS program.[21]

As in all *ab initio* electronic computations, when choosing a computational method, a trade-off must be made between computational convenience and ultimate achievable accuracy. This principle, of course, applies to the problem of geometry optimization. The computationally most facile approaches are the SCF and MP2 optimizations, which are limited to single determinantal ground states; CASSCF optimizations, which include nondynamical correlation and may be applied to excited states but often with convergence difficulties; and the IVO-CASCI method described here, which has the same range of applicability as CASSCF treatments but without convergence difficulties. Because these methods for geometry optimization require at least an order of magnitude less computer time than the various coupled cluster approaches, a meaningful test of the IVO-CASCI geometry optimization involves comparison with the other computationally facile methods. However, for completeness, coupled cluster calculations are also included in the comparison.

Section II provides a brief outline of the scheme for

generating the improved virtual orbitals along with relevant equations describing the IVO scheme, and the calculated results are presented and compared with other methods in the subsequent section. The calculated ground state geometries for the Be_2, LiF, H_2S, and HCN molecules are generally comparable or superior to those of the SCF, CASSCF, MP2, CASCI (with canonical HF orbitals), and CCSD (sometimes even the CCSDT) methods, as are the ground state vibrational frequencies. Excited state geometries and frequencies for HCN outperform those from CASSCF. The inclusion of nondynamical contributions is clearly responsible for the improved behavior of the IVO-CASCI method over the single reference SCF and MP2 methods for these molecules, while the improvement over the CASSCF results is suggestive that the energy derivatives are more accurately described when the CAS better represents the low lying electronic states, as in the IVO-CASCI approach, rather than when the CAS is oriented towards describing correlation in one (or the average of a few) specific states as in the CASSCF approach.

II. GENERATION OF IMPROVED VIRTUAL ORBITALS

One portion of the CASSCF procedure effectively involves a CASCI computation using orbitals optimized for a single state or for some weighted average of several states. A CI computation of dimension D is well known to provide rigorous upper bounds to the energies of the D lowest electronic states,[22] but, of course, accurate bounds are expected only for the lowest few of these states, which, fortunately, are generally the states of interest. However, the use of orbitals optimized for one (or for the average of a few) states generally yields a poor representation of the other states, and this feature is partially responsible for the poor convergence of the CASSCF procedure as the dimension of the CAS grows. Our alternative approach involves directly choosing orbitals that simultaneously provide a good representation for several of the lowest lying electronic states. This procedure is followed in H^v computations in which the CAS orbitals are defined as comprising the highest occupied orbitals (perhaps, only for certain symmetries) in the SCF approximation to the ground (or a low lying) state and a set of the lowest lying IVO orbitals constructed from the remaining unoccupied space in the basis set. This approach is designed to maximize the accuracy of the first order H^v approximation, which is equivalent to a CASCI, for the low lying electronic states in order to minimize the required perturbative corrections.[8] Earlier H^v computations use a computationally complex sequence of SCF computations to obtain the IVOs, but more recently they employ a simple direct method for generating the IVOs for several common situations.[18] The significant improvement in computational efficiency for determining the IVOs is one important feature contributing to the packageability of the IVO-CASCI method and its use for geometry optimization.

Since the basic philosophy of generating the IVOs is the same for both restricted and unrestricted HF orbitals, we only present the restricted HF case, which is used herein.

A. Closed-shell ground state

When the ground state of the system is a closed shell, we begin with the Hartree-Fock (HF) molecular orbitals (MOs) for the ground state wave function, $\Phi_0 = \mathcal{A}[\phi_1 \bar{\phi}_1 \phi_2 \bar{\phi}_2 \cdots \phi_n \bar{\phi}_n]$, where $\mathcal{A}$ is the antisymmetrizer. Let the indices $i, j, k, \ldots$ refer to the occupied HF MOs $\{\phi_i\}$ and $u, v, w, \ldots$ to unoccupied HF MOs. All the HF MOs are determined by diagonalizing the one electron Hartree-Fock operator ^1F,

$$^1F_{lm} = \langle \phi_l | H + \sum_{k=1}^{occ} (2J_k - K_k) | \phi_m \rangle = \delta_{lm} \epsilon_l, \tag{1}$$

where l and m designate any (occupied or unoccupied) HF MO and ϵ_l is the HF orbital energy. The operator H is the one-electron portion of the Hamiltonian, and J_k and K_k are Coulomb and exchange operators, respectively, for the occupied orbital ϕ_k.

An excited state HF computation would provide a new set $\{\chi\}$ of MOs that produce the lowest possible energies for the low lying singly excited $\Psi_{\alpha \to \mu}$ state,

$$\Psi(\alpha \to \mu) = \mathcal{A}[\chi_1 \bar{\chi}_1 \chi_2 \bar{\chi}_2 \cdots (\chi_\alpha \bar{\chi}_\mu \pm \chi_\mu \bar{\chi}_\alpha) \cdots \chi_n \bar{\chi}_n], \tag{2}$$

corresponding to an excitation of an electron from the orbital χ_α to χ_μ, where the $+$ and $-$ signs correspond to triplet and singlet states, respectively. The new MOs $\{\chi_\alpha\}$ and $\{\chi_\mu\}$ may be expressed as a linear combination of the ground state MOs $\{\phi_i, \phi_u\}$. If, however, the orbitals are restricted such that the $\{\chi_\alpha\}$ are linear combinations of only the occupied ground state MOs $\{\phi_\alpha\}$ and the $\{\chi_\mu\}$ are expanded only in terms of the unoccupied $\{\phi_u\}$,

$$\chi_\alpha = \sum_{i=1}^{occ} a_{\alpha i} \phi_i, \quad \chi_\mu = \sum_{u=1}^{unocc} c_{\mu u} \phi_u, \tag{3}$$

then the new orbital set $\{\chi_\alpha, \chi_\mu\}$ not only leaves the ground state wave function unchanged but also ensures the orthogonality and applicability of Brillouin's theorem between the HF ground state and the $\Psi_{\alpha \to \mu}$ excited states. In addition, this choice also benefits from using a common set of MOs for the ground and excited states, a choice which simplifies the computation of oscillator strengths, etc. However, we avoid the computationally laborious reoptimization of the occupied orbitals by setting $\{\chi_\alpha\} \equiv \{\phi_\alpha\}$, i.e., by choosing $a_{\alpha j} = \delta_{\alpha j}$, thereby simplify enormously the procedure for generating the IVOs. Hence, the coupled equations determining the coefficients $a_{\alpha j}$ and $c_{\mu \nu}$ reduce to a single eigenvalue equation of the form $F'C = C\Gamma$, where the operator F' is given by

$$F'_{vw} = {}^1F_{vw} + A^\alpha_{vw}, \tag{4}$$

where ^1F is the ground state Fock operator and the additional term A^α_{vw} accounts for the excitation of an electron out of orbital ϕ_α,

TABLE I. Basis sets used for Be_2, LiF, H_2S, and HCN molecules.

Atom	Basis
LiF	cc-pVQZ
Be_2	6-311++G($3df, 3pd$)
H_2S	cc-pVTZ
HCN	aug-cc-pVDZ

$$A^\alpha_{vw} = \langle \chi_v | -J_\alpha + K_\alpha \pm K_\alpha | \chi_w \rangle. \tag{5}$$

The minus sign in Eq. (5) applies for $^3\Psi_{\alpha \to \mu}$ a triplet state, while the plus sign is for the singlet $^1\Psi_{\alpha \to \mu}$ state.[12,16] The corresponding transition energy is

$$^{1,3}\Delta E(\alpha \to \mu) = E_0 + \gamma_\mu - {}^1F_{\alpha\alpha}, \tag{6}$$

where E_0 is the HF ground state energy and γ_μ is the eigenvalue of $F'C = C\Gamma$ for the μth orbital.

Special care is required for systems where the highest occupied HF MOs are doubly degenerate. In order that the $\{\chi_\mu\}$ retain molecular symmetry, the construction of F' must be modified from Huzinaga's scheme. If ϕ_α and ϕ_β are the highest occupied degenerate HF MOs, then the matrix element A^α_{vw} in Eq. (5) is replaced for these degenerate systems by $A^{\alpha,\beta}_{vw}$, where

$$A^{\alpha,\beta}_{vw} = \tfrac{1}{2} \langle \chi_v | -J_\alpha + K_\alpha \pm K_\alpha | \chi_w \rangle$$
$$+ \tfrac{1}{2} \langle \chi_v | -J_\beta + K_\beta \pm K_\beta | \chi_w \rangle. \tag{7}$$

III. RESULTS AND DISCUSSION

Unless otherwise noted, the basis sets employed in these calculations are listed in Table I. The geometry optimization is effected by interfacing the IVO-CASCI method into the GAMESS program which also supports numerical gradient calculations for the CCSD scheme. The SCF and MP2 optimized geometries and vibrational frequencies are also computed using GAMESS, whereas the CASSCF data are obtained using the DALTON package.[23] We emphasize that all the schemes except CCSD and IVO-CASCI compute energy derivative analytically and hence execution times are not compared.

A. LiF

The equilibrium bond length for the $X\,^1\Sigma$ state of LiF is determined within the cc-pVQZ basis set.[24] The CASSCF and IVO-CASCI geometry optimizations are performed with a (10,10) CAS. The CCSD method provides the most accurate estimate of the equilibrium bond length for the ground state (see Table II). The geometries and vibrational frequencies obtained from SCF and IVO-CASCI geometry optimizations are almost identical and deviate from experiment by only 0.01 Å. The CASSCF and MP2 methods offer more accurate estimates of the vibrational frequency than for the equilibrium bond length, but the SCF and IVO-CASCI frequencies are too high by $\sim$37 cm^{-1}.

TABLE II. Ground state equilibrium bond lengths (in Å) and vibrational frequency (ω in cm^{-1}) of LiF and Be$_2$.

Method	LiF		Be$_2$	
	R_e	ω	R_e	ω
Expt.	1.564[a]	910[b]	2.46[c]	275.8[c]
RHF	1.553	949	5.52	47
IVO-CASCI	1.553	946	2.42	281
CASSCF	1.578	904	1.88	599
MP2	1.582	899	2.77	101
CCSD	1.563		4.40	
MRCI[d]			2.44	269.9
CCSDT[e]			2.65	
IVO-CASCI[f]			2.30	

[a]Reference 35.
[b]Reference 36.
[c]Reference 30.
[d]Reference 31.
[e]Reference 37.
[f]From the same basis set as used in CCSDT (Ref. 28).

B. Be$_2$

The valence configuration of the Be$_2$ ground state is $(2\sigma_g)^2(2\sigma_u)^2$, with an equal number of bonding and antibonding electrons. This indicates a lack of tendency for bond formation between the two ground state Be atoms. However, weak bonding is expected to arise due to the near degeneracy of $2s$ and $2p$ orbitals. Thus, the ground state geometry of Be$_2$ has been the subject of several theoretical studies,[25] including the restricted Hartree-Fock (RHF) calculations of Whiteside et al.,[26] the CI work of Bender and Davidson,[27] the coupled electron pair-approximation study of Dykstra et al.,[28] and the relativistic calculations of Malli and Oreg.[29] Among these studies, Dykstra et al. find binding for the ground state of Be$_2$, while the CI calculation of Bender and Davidson exhibits a shallow minimum in the potential energy curve. The RMP4(SDQ)/6-31G* calculations of Whiteside et al. estimate the Be–Be bond length to be 3.999 Å, which is 1.6 times the experimental bond length of 2.46 Å.[30] Computationally expensive CCSDT calculations of Sosa et al. estimate the R_e of Be$_2$ to be 2.65 Å (from a $7s3p1d$ basis),[28] which deviates by 0.19 Å from experiment. (In contrast, IVO-CASCI calculations with the same basis underestimate the Be$_2$ equilibrium bond length by 0.16 Å.) A subsequent MRCI treatment by Gdanitz[31] obtains the most accurate estimates of $R_e = 2.44$ Å and $\omega_e = 269.9$ cm^{-1}.

The ground $X\,^1\Sigma_g^+$ state geometry of Be$_2$ is optimized using the 6-311++G($3df, 3pd$) contracted Gaussian basis of Krishnan et al.[32] Table II compares the equilibrium bond length and vibrational frequency of the ground state of the Be$_2$ molecule, computed using various perturbative and nonperturbative schemes. The complete active space used in the CASSCF and IVO-CASCI calculations is constructed from eight active electrons and nine active orbitals ($4\sigma_g$, 3σ, $1\pi_u$). As evident from Table II, the IVO-CASCI approach is the only one of the *computationally facile* methods that provides a reasonably accurate estimate of the ground state bond length and vibrational frequency. (The CCSD treatment takes

TABLE III. $X\,^1A_1$ state equilibrium bond lengths (in Å) and vibrational frequencies (ω in cm^{-1}) of H$_2$S.

Method	R_e	$\angle$HSH	ω_1	ω_2	ω_3
Expt.[a]	1.328	92.2	2615	1183	2628
RHF	1.330	94.2	2844	1319	2853
MP2	1.335	92.2	2771	1217	2790
IVO-CASCI	1.346	92.6	2668	1263	2669
HF-CASCI	1.344	100.5	2666	1542	2710
CASSCF	1.334	91.7	2792	1226	2852
CCSD	1.330	94.2	2803	1208	2821

[a]Reference 38.

at least order of magnitude more CPU time than the IVO-CASCI calculation.)

C. H$_2$S

The ground and excited state properties of H$_2$S have been extensively studied both theoretically and experimentally. The system is sufficiently complex for benchmarking the ability of the IVO-CASCI method for describing the ground state geometry and vibrational frequencies. We employ a cc-pVTZ basis for the sulfur and hydrogen atoms and a CAS comprising six active electrons (in the $5a_1$, $2b_1$, and $2b_2$ orbitals) and seven active orbitals ($5\text{–}7a_1$, $2\text{–}3b_1$, and $2\text{–}3b_2$).

Table III compares the optimized ground state geometry and vibrational frequencies obtained from the IVO-CASCI scheme with experiment and with other calculations. The IVO-CASCI calculation offers the most accurate estimate of the ground state vibrational frequencies, while slightly overestimates the S–H bond distance by 0.02 Å but reproducing the HSH bond angle quite accurately. The bond distances and bond angles are better described in the MP2 approach, but the MP2 stretching frequencies deviate significantly from experiment. The geometrical parameters obtained from the CCSD and CASSCF schemes exhibit similar trends. CASCI calculations with canonical HF orbitals (HF-CASCI) offer reasonably accurate estimates of S–H bond lengths and the corresponding stretching frequencies, but the scheme, however, fails to reproduce the HSH bond angle and the corresponding bending frequency.

D. HCN

The hydrogen cyanide (HCN) molecule has been the subject of several experimental and theoretical investigations and, thus, is ideal for developing and testing models designed to compute electronic and rovibrational properties of electronically excited states because the ground and excited state properties of HCN are well documented in the literature. Moreover, interest in HCN has recently been heightened among astrophysicists due to the detection of HCN in the atmosphere of Titan[33] and of Carbon stars.[34]

The optimized geometries for HCN from each of the theoretical methods are presented in Table IV. The calculations all use the aug-cc-pVDZ (Ref. 24) Gaussian basis set. The CAS for both the CASSCF and IVO-CASCI geometry optimizations comprises ten active orbitals and eight active

TABLE IV. Ground and excited state geometrical parameters of HCN. Bond lengths and bond angles are given in Å and deg, respectively.

State	Method	R(CH)	R(CN)	$\angle$HCN
$X\,^1A_1$	Expt.[a]	1.064	1.156	180.0
	RHF	1.057	1.125	180.0
	IVO-CASCI	1.078	1.156	180.0
	HF-CASCI	1.066	1.155	180.0
	CASSCF	1.085	1.169	180.0
	MP2	1.065	1.167	180.0
	CI	1.055	1.180	180.0
	CCSD	1.079	1.168	180.0
	IVO-CASCI[b]	1.067	1.155	180.0
	HF-CASCI[b]	1.063	1.157	180.0
	CCSD[b]	1.065	1.149	180.0
$1\,^1A''$	Expt.[a]	1.14	1.297	125.0
	IVO-CASCI	1.137	1.293	125.2
	HF-CASCI	1.116	1.288	125.2
	CASSCF	1.14	1.331	119.4
	CI	1.096	1.318	127.2
$3\,^1A'$	Expt.[a]	1.14		141.0
	IVO-CASCI	1.082	1.245	138.0
	HF-CASCI	1.113	1.252	134.5
	CASSCF	1.138	1.278	136.5
	CI	1.092	1.264	141.2

[a]Reference 38.
[b]From cc-pVQZ basis.

electrons. Tables IV and V demonstrates that the IVO-CASCI predicted geometries and vibrational frequencies for the ground $^1\Sigma^+$ state of HCN are in close agreement with experiment. The MP2 method offers a reasonably accurate estimate of the vibrational frequencies and C–H bond distance, but its predicted C–H bond length differs by 0.008 Å from experiment. The CASSCF and CCSD methods overestimate both the C–H and C–N bond lengths, and the CASSCF vibrational frequencies are high. The excited state geometrical parameters are also well reproduced in the IVO-CASCI approach, apart from the C–H bond length of the $1\,^3A'$ state which is in error by 0.05 Å.

Table IV also presents the ground state geometrical parameters obtained using the larger cc-pVQZ (Ref. 24) Gaussian basis set to indicate the variation due to basis set extension. Table IV indicates that the larger cc-pVQZ basis set calculation improves the accuracy of the CCSD and IVO-CASCI predicted C–H and C–N bond distances. Interestingly, the geometrical parameters from the IVO-CASCI (and the HF-CASCI) calculation with the cc-pVQZ basis are more accurate than from the CCSD.

TABLE V. Ground state vibrational frequencies (in cm^{-1}) of HCN.

Method	C–H stretch	C–N stretch	H–C–N bend
Expt.[a]	3312	2098	714
RHF	3631	2410	878
MP2	3476	1998	704
CASSCF	3570	2133	765
IVO-CASCI	3287	2137	764
HF-CASCI	3418	2152	741

[a]Reference 38.

IV. CONCLUSIONS

The IVO-CASCI method is extended to enable geometry optimization and the calculation of vibrational frequencies for the ground and excited states using numerical energy gradients. With few exceptions, the calculated ground state geometries for the Be_2, LiF, H_2S, and HCN molecules are generally comparable or superior to those of the SCF, CASSCF, MP2, and even the CCSD methods as are the ground state vibrational frequencies. The accurate IVO-CASCI estimate for the notoriously difficult Be_2 bond length and vibrational frequency is significant since all other computationally *inexpensive* approaches produce poor results for this system. Excited state geometries and vibrational frequencies for HCN outperform those from CASSCF, thereby demonstrating the viability of the IVO-CASCI scheme for excited state geometry optimization. While the accuracy of the IVO-CASCI and HF-CASCI predicted geometries and frequencies is comparable in certain cases, in general, the IVO-CASCI offers a more reliable estimate of the computed quantities.

The inclusion of nondynamical contributions is clearly responsible for the improved behavior of the IVO-CASCI method over the single reference SCF, MP2, and CCSD methods for these molecules, while the improvement over CASSCF results is suggestive that energy derivatives are more accurately described when the CAS better represents the low lying electronic states, as in the IVO-CASCI approach, than when the CAS is oriented towards describing correlation in one (or a few) specific states as in the CASSCF method. Moreover, the IVO-CASCI scheme involves no self-consistent field iterations beyond an initial restricted self-consistent field calculation at each geometry and thus is not susceptible to the convergence problems that often plague the CASSCF approach. In addition, while not detailed herein, accurate geometries are generally obtained using smaller reference spaces for the IVO-CASCI treatments than for CASSCF calculations, although the description of vibrational frequencies requires the use of comparable sized CASs for both methods. Hence, it will be worthwhile to implement the analytical derivative formulation of the IVO-CASCI method.

The numerical gradient procedure is computationally expensive because the energy is computed *twice* along each of the totally symmetric modes (backward and forward displacements). The computation of vibrational frequencies is even costlier in this scheme. For example, 81 single point energies are computed to calculate the vibrational frequencies of HCN. The numerical treatment of energy gradients, though computationally expensive, has been used here as a prelude to test the IVO-CASCI geometry optimization before coding the analytical gradient version. The high quality results from the numerical approaches provide strong impetus for coding the analytical treatment.

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