Table 21 Calculated Electron Affinities and Electron Detachment Energies (eV) of Linear C_4 and C_4^-[a]

Basis set	Method	VEA	AEA	VEDE
5s4p1d	UHF-CCSD	3.30		3.57
5s4p1d	UHF-CCSD+T(CCSD)	3.39		3.62
PVTZ	UHF-MBPT(2)	3.982	4.074	4.170
PVTZ	UHF-CCSD	3.482	3.628	3.779
PVTZ	ROHF-MBPT(2)	3.561	3.660	3.764
PVTZ	ROHF-CCSD	3.525	3.669	3.817
PVTZ	UHF-MBPT(2)	3.924	4.020	4.155
PVTZ	UHF-CCSD	3.442	3.579	3.738
PVTZ	UHF-CCSD+T(CCSD)	3.553	3.647	3.807
PVTZ	UHF-CCSD(T)	3.555	3.654	3.812
PVTZ+sp	UHF-MBPT(2)			4.288
PVTZ+sp	UHF-CCSD			3.852
PVTZ+sp	UHF-CCSD+T(CCSD)			3.933
PVTZ+sp	UHF-CCSD(T)			3.937
5s4p2d1f	UHF-CCSD			3.775
5s4p2d1f	UHF-CCSD+T(CCSD)			3.855
5s4p2d1f	UHF-CCSD(T)			3.860

[a] Reference 119.

In addition to the basis, the very important effect of triple excitations for obtaining highly accurate answers is apparent from this set of calculations.

Just as a spectrum of different ionizations is commonly observed, several bound electron attached states may exist. This can happen for a cation like MgF$^+$ because of the net positive charge. In an independent particle picture, different empty orbitals (see Figure 15) can be occupied at different E_{A_i} to give the corresponding electronic states of the neutral (see Table 22). These are the same states that could be obtained via electronic excitations of the neutral, but they also can be approached as an electron attachment problem using either EOM-CC or FS-MRCC. An electron adding to the 7σ orbital gives the $X^2\Sigma^+$ state of MgF; adding one to the 3π orbital gives the $A^2\Pi$ state, and adding one to the 8σ and 9σ orbitals provides the B and $C^2\Sigma^+$ states, respectively.

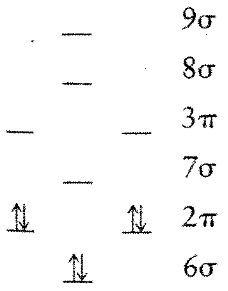

Figure 15 Orbital diagram of *MgF*$^+$($1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 6\sigma^2 2\pi^4$).

Table 22 Electronic Transition Energies (cm^{-1}) of MgF^+

	$A^2\Pi \leftarrow X^2\Sigma^+$	$B^2\Sigma^+ \leftarrow X^2\Sigma^+$	$C^2\Sigma^+ \leftarrow X^2\Sigma^+$
FSMRCCSD[a]	29,312.4		
QRHF-CCSD[a]	29,378.7		
FSMRCCSD[b]	27,851.2	37,831.4	45,537.5
Experimental	27,852.5	37,187.4	42.589.6

[a] Mg: 6-31G*, F: DZP, total: 35 Gaussian-type orbitals (GTOs).
[b] Mg: (12s9p12d/8s6p4d), F: (10s7p5d/6s5p4d), total: 95 GTOs.

ELECTRONIC SPECTRA

In electronic spectroscopy, processes that involve transitions between two distinct electronic states in atoms and molecules are studied. The energy typically required for these processes falls in the ultraviolet or visible range of the electromagnetic spectrum; the field is therefore also frequently called ultraviolet/visible (or UV/vis) spectroscopy. Due to availability of the requisite technology, this is the oldest branch of chemical spectroscopy and has been of interest to quantum chemists since the late 1920s. Indeed, many of the early successes of Mulliken's molecular orbital theory involved qualitative interpretations of electronic spectra. The advent of the Hückel molecular orbital treatment in the 1930s made semiquantitative calculations for conjugated organic molecules possible for the first time.[120] Two decades later, the semiempirical crystal field model was developed and applied with great success to calculate electronic energy levels in transition metal complexes.

Much of our qualitative understanding of electronic transitions and the language we use to describe them ultimately derives from the independent particle approximation. Typically, we interpret features in absorption spectra as "$n \rightarrow \pi^*$" or "$\sigma \rightarrow \sigma^*$" transitions, etc., in an attempt to describe these processes in terms of the simplest molecular orbital picture. However, we should be aware that the molecular orbital paradigm is approximate and that the actual excitation process is more complex. Within the Born–Oppenheimer approximation, the interaction between specific wavelengths of UV or visible radiation and molecules leads to transitions between quantum states that "belong" to two separate potential energy surfaces. In general, the absorption of a photon takes a state characterized by distinct electronic, vibrational, and rotational quantum numbers to another state having another set of quantum numbers. The energy required for transitions between different electronic states is typically much larger than spacings between vibrational and rotational states, so typically observed low resolution spectra are often characterized by blobs that grossly represent the electronic part of the transition, with the underlying vibrational and rotational features unresolved. Nevertheless, spectra having sufficiently good resolution often show vibrational and rotational "fine structure," with transitions between individual states visible within the absorption envelope. (The modern techniques of supersonic jet expansion and laser spectroscopy allow very high resolution spectra to be obtained, even for relatively large organic molecules.) These features are often useful for determining differences in equilibrium geometry between the ground and excited states of the molecule and other properties. Our objective here is to survey some methods that can be used to calculate energy differences between the adiabatic potential energy surfaces obtainable from quantum chemical calculations.

As in our discussion of photoelectron spectroscopy, a simple and conceptually appealing description of the excitation process can be developed as follows. We will assume that the molecular orbital picture is a valid first-order approximation and that the radiation field causes a single electron to be promoted from the occupied spin orbital *i* to orbital *a*, which is not occupied in the ground electronic state. Furthermore, in this simplest model we further require that the molecular orbitals in the ground and excited states must be the same. This treatment, which is based on a one-electron picture that neglects orbital relaxation effects, is the direct analog of Koopmans' theorem but for excitation processes. Evaluating the excited state expectation value for the single excitation Φ_i^a and for the Hartree–Fock ground state Φ_0, we obtain after some simplification,

$$\Delta E = \langle \Phi_i^a | H | \Phi_i^a \rangle - \langle \Phi_0 | H | \Phi_0 \rangle = \epsilon_a - \epsilon_i + \langle ai \| ai \rangle \qquad [63]$$

Note that unlike the simple Hückel method, this SCF-based approach does not predict that the excitation energy is given by a difference of orbital eigenvalues. Rather, this model allows for a certain amount of interaction between electrons and correctly predicts unequal energies for configurations that differ only in the spin of unpaired electrons. In the case that the ground state is a closed-shell singlet, this model predicts singlet and triplet excitation energies of

$$\Delta E_{\text{singlet}} = \epsilon_a - \epsilon_i + \langle ai | ai \rangle = \epsilon_a - \epsilon_i + (aa|ii) \qquad [64]$$

and

$$\Delta E_{\text{triplet}} = \epsilon_a - \epsilon_i + \langle ai | ai \rangle - \langle ai | ia \rangle = \epsilon_a - \epsilon_i + (aa|ii) - (ai|ai) \qquad [65]$$

The last terms of Eqs. [64] and [65] use the familiar Mulliken two-electron integral notation. Note that the singlet–triplet splitting predicted by this simplest model is given by the exchange integral between orbitals *a* and *i*. Since this term is always positive, the simple model presented here predicts that the triplet state is more stable, thereby providing a simple physical justification for Hund's rule.

Although the model described above may be qualitatively appealing, it does not provide quantitatively satisfactory predictions of excitation energies even though the analogous Koopmans approximation works reasonably well for ionization potentials. Why should this be? The principal difference between the Koopmans approximation for ionization potentials and the present treatment of excitation energies is that the latter explicitly involves unoccupied SCF orbitals. This is the main problem with these calculations, inasmuch as the SCF procedure does not optimize the virtual orbitals and the frozen orbital approximation fails.

It is natural to ask whether a better theoretical approach to excitation processes exists, which does not discard the intuitively attractive one-electron picture. Indeed, such a method was invented nearly a half-century ago and is known as the Tamm–Dancoff approximation (TDA) or CI singles (i.e., CIS).[121] In this approach, the excited state is approximated by a linear combination of elementary frozen-orbital single excitations. TDA exploits a standard CI procedure. First, we take the set of single excitations and construct $\langle S|H|S\rangle = H_{ss}$ and solve $H_{ss}C_k = C_kE_k$. The eigenvalues of this matrix, E_k, represent the eigenvalues of the Schrödinger equation for excited states subject to the restrictions defined by the model, and the eigenvectors are the associated wavefunctions. The excitation energy is $E_k - E_{SCF}$, because single excitations do not mix with the UHF or RHF solution, Φ_0; the ground state energy is $E_0 = E_{SCF}$. In some respects, the term CIS is unfortunate because it suggests a method that offers some treatment of electron correlation effects. In fact, the terms "CI" and "electron correlation" are so often used interchangeably in the literature that it may be difficult to understand that a method called CIS completely neglects electron correlation! Hereafter, we will refer to this method as the TDA, with the understanding that is equivalent to CIS. (Both the ACES II and GAUSSIAN program systems have capabilities for performing TDA calculations.)

The discussion of orbital relaxation in the preceding section provides us with a clear way of understanding the shortcomings of the TDA. Recall that any Slater determinant formed from a particular set of basis functions may be obtained from any other Slater determinant that lies in the same basis by means of the exponential transformation

$$|\Phi'\rangle = \exp(T_1)|\Phi_0\rangle \qquad [66]$$

Let us now assume that the excited state wavefunction is given exactly by some Slater determinant. It should be clear that the TDA does not contain sufficient flexibility to describe this state in the general case because the excited state wavefunctions in this approximation are given by a linear combination of singly excited determinants

$$|\Phi^{TDA}_{excited}\rangle = \hat{C}_1|\Phi_0\rangle \qquad [67]$$

The flexibility missing from the TDA arises from its neglect of nonlinear terms in the exponential operator of Eq. [66], which would lead to the inclusion of very specific types of determinants "doubly," "triply" excited, etc., into the parameterization of the single determinant $|\Phi'\rangle$. It is very important to understand that $|\Phi'\rangle$ is still a single configuration wavefunction and that this inclusion of more highly excited determinants therefore is not an electron correlation effect. [This discussion is somewhat oversimplified for excited states that correspond to low spin electron configurations, such as open-shell singlets. In these cases, the "simplest" excited state wavefunction that retains the property of being a spin eigenfunction is $|\Phi_{\text{excited}}\rangle = 1/\sqrt{2}[\phi^{\alpha}_{i\to a} + \phi^{\beta}_{i\to a}]$, where $\phi^{\alpha}_{i\to a}$ and $\phi^{\beta}_{i\to b}$ are Slater determinants differing only in the spin of the excited electron. Within the Thouless parameterization, these determinants may be written as $\exp(T_1^{\alpha})|\Phi_0\rangle$ and $\exp(T_1^{\beta})|\Phi_0\rangle$, respectively. Nevertheless, the resulting excited state wavefunction corresponds to a single electronic configuration and contains no correlation.] After one understands the considerations above, it can be seen that the first way to improve the TDA is to extend its flexibility through a better treatment of the $\exp(T_1)$ operator. These effects are included, albeit in an approximate and somewhat indirect way, in what is called the *random phase approximation* (RPA).[121] [Again, to satisfy requirements of spin symmetry, we take $\exp(T_1)$ to be $\exp(T_1^{\alpha} + T_1^{\beta}) = \exp(T_1^{\alpha})\exp(T_1^{\beta})$ in the following.]

We can derive this method in a nonstandard way[32] by considering the energy associated with $\Phi' = \exp(T_1)\Phi_0$, that is,

$$E = \frac{\langle\Phi'|H|\Phi'\rangle}{\langle\Phi'|\Phi'\rangle} = \frac{\langle\Phi|\exp(T_1^{\dagger})H\exp(T_1)|\Phi\rangle}{\langle\Phi|\exp(T_1^{\dagger})\exp(T_1)|\Phi\rangle}$$

and vary the energy with respect to $T_1^{\dagger}$, which leads us to the matrix equation that depends on the $\mathbf{H}_{ss}$ matrix, that is, the **A** matrix of RPA augmented by the **B** matrix $(\langle\Phi|H\hat{T}_1^2/2|\Phi\rangle)$ that derives from quadratic T_1 terms. This alternative approach to the calculation of excitation energies allows for some effects of selected doubly excited configurations, and the RPA method is therefore somewhat more flexible than the TDA. It is often stated in the literature that the RPA method (which is equivalent to the time-dependent Hartree–Fock approximation) reduces to the coupled–perturbed Hartree–Fock approximation in the static case and contains electron correlation effects, but this is certainly untrue unless one adopts a nonstandard view of what is meant by correlation.

Excitation energies calculated with the RPA and TDA approaches for N_2 with a moderately large basis set are listed in Table 23. Both the RPA and TDA excitation energies are significantly lower than those obtained with the simplest frozen orbital approximation. All these approaches differ only in their treatment of the final state, and the pattern of predicted excitation energies shows this in a rather dramatic way. Both the RPA and TDA allow for a limited amount of relaxation and provide much improved predictions. Inclusion of the

Table 23 Excitation Energies for N_2 (5s3p1d Basis)

	Excitation energies (eV)		
Final state	TDA	RPA	Experimental
$a'^1\Sigma_u^-$	8.50	7.93	9.9
$\omega^1\Delta_u$	9.08	8.80	10.3
$a^1\Pi_g$	9.99	9.74	9.3
$b'^1\Sigma_u^+$	15.78	15.48	14.4

special "double" excitation effects discussed above in the RPA is reflected in a systematic lowering of the predicted excitation energies relative to the TDA.

Before concluding this discussion of the TDA and RPA approaches, one problem occasionally encountered in RPA calculations of excitation energies relative to a closed-shell ground state should be discussed. Within the RPA, excitation energies are intimately related to the dependence of the energy with respect to infinitesimal changes in the molecular orbitals. In some cases, Hartree–Fock solutions are "unstable," meaning that a small change in the orbitals results in a lowering of the electronic energy. Most frequently, the change that lowers the energy involves a breaking of the spin symmetry of α and β orbitals. Hence, the determinant is transformed from an RHF to a UHF wavefunction. The UHF energy is always lower than or equal to the RHF result because spin symmetry can be relaxed. If lower energy UHF solutions exist, we say the RHF is unstable. When this occurs, the RPA fails and predicts imaginary excitation energies for transitions to triplet excited states. The subject of Hartree–Fock instabilities is rather complicated and takes us too far afield from our discussion, but suffice it to say that these phenomena tend to occur in systems that are poorly described by a single determinant. Hence, in cases that should be suitable for the RPA (both ground and excited states are well represented by a single configuration), these pathological problems will not occur. However, this sort of instability is actually encountered fairly often; a simple example is C_2H_4. It should be expected to occur in any closed-shell system for which one can draw reasonable Lewis dot structures with two unpaired electrons such as for ozone (Figure 16). Molecules that fall into this category are frequently called *biradicals*. The nature of these systems and the problems associated with their theoretical description form an interesting subject, which is not discussed here.

A second type of instability is known as a "singlet" instability, which

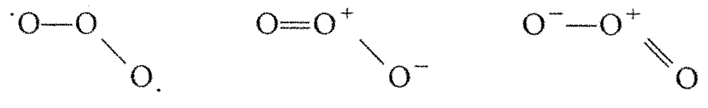

Figure 16 Resonance in ozone.

means that the SCF energy can be lowered by an in-phase rotation of α and β spin orbitals (i.e., there is a lower energy single determinant that is still a closed-shell singlet). This type of instability is not very common and is usually encountered only in exotic systems such as N_2 at very large internuclear separations and the anion O_2^{2-}. Fortunately, one is usually more interested in singlet excitation energies, and the scarcity of cases exhibiting this type of instability means that the RPA can usually be used for such studies.

When it is possible to describe an excited state by a single configuration wavefunction, the "best" uncorrelated approach would be via separate evaluation of SCF wavefunctions for both the ground and excited states. Subtraction of the resulting energies gives us excitation energies in a ΔE_{SCF} treatment analogous to that discussed previously for ionization potentials. However, the ΔE_{SCF} approach to excited states has a number of undesirable features that severely limit its applicability. First, most excited states cannot be adequately approximated by any single determinant (many are open-shell singlets), and one must resort to low spin ROHF approaches, which can be difficult to converge. Second, as in the case of ionization potentials, one encounters the problem of variational collapse. In fact, this represents even a greater problem in excitation energies than it does in the determination of ionization potentials because in the latter case we can at least determine the lowest ionization potential in this manner. In general, the same is not true for excitation energies. Consider a molecule with no elements of symmetry, such as FOOH. In such a case, it may not be possible to routinely obtain SCF solutions for any state other than the electronic ground state, prohibiting any attempt to calculate ΔE_{SCF} excitation energies.

Another desirable aspect of using the TDA and RPA approaches is that they both use a common set of molecular orbitals, which aids both in developing qualitative interpretations of the excitation process and also in calculating properties such as transition moments. The latter depends on $|\langle\psi_i|\mathbf{r}|\psi_f\rangle|^2$, where $\mathbf{r} = \Sigma_j\mathbf{r}_j$ is the dipole operator. It is easy to evaluate such a one-electron property provided ψ_i and ψ_f are described in terms of the same orthonormal orbital set. When different orbitals are used in ψ_i and ψ_f—typically to get the "best" possible solution for both states—the resultant nonorthogonality causes a number of complications. This is particularly true when an entire spectrum of electronic states is the objective and all transition moments are required. Nevertheless, all the methods discussed so far neglect electron correlation effects, and one must go beyond the single configuration approximation if quantitative accuracy is to be achieved.

Conceptually, one of the simplest ways to study excited states at the correlated level of theory is by means of ΔE methods, in which E is obtained with some post-HF method. While the problems of variational collapse discussed above severely complicate efforts to calculate excitation energies by ΔSCF methods, it is actually straightforward to obtain ΔCI excitation energies, provided the same reference function is used for both states. In this case, the orbitals are usually optimized for the ground state. Correlated energies are then obtained by diagonalization of the Hamiltonian matrix in the basis of the reference determinant and some suitable subset of excited configurations. In this way, wavefunctions for the ground and excited states as well as excitation energies are easily obtained. Despite the conceptual simplicity of this approach, it is not often used in practice. Why is this? Once again, considerations of orbital relaxation come into play. Remember that all the CI wavefunctions are based on a common reference state, Φ_0, for each k, and that the orbitals making up Φ_0 are typically optimized for the ground state. Since computational considerations limit practical ΔCI approaches to the CISD approximation, insufficient orbital relaxation is included, and therefore the excited state is not described as well as the ground state. As a result of the unbalanced nature of the approach, ΔCISD excitation energies typically overestimate excitation energies; especially large differences can be expected to occur when the best one-electron descriptions (natural orbitals) for the ground and excited states are very different. In fact, TDA and RPA calculations are usually preferable to ΔCI because these approaches offer a more balanced description of the ground and excited states.

The "orbital problem" associated with ΔCI calculations can be circumvented by a number of means. First, modern developments in MCSCF orbital optimization strategies have made obtaining MCSCF solutions for both ground and excited states a fairly routine matter. In some calculations, the orbitals are indeed optimized for each state of interest, and the ground and excited states are treated in an even-handed way. Dynamic correlation can then be included by performing multireference configuration interaction calculations. This approach, which can be used to obtain very accurate excitation energies, has been used to study a number of small molecules. However, it is inconvenient for the study of several excited states because separate orbital optimizations and CI calculations are required for each state. Furthermore, the use of different orbitals for different states severely complicates the calculation of transition properties, which are needed to describe important physical phenomena such as oscillator strengths.

One way to include many of the advantageous features of both the ΔCI and ΔMCSCF-CI approaches is to use "state-averaged" orbitals. In these calculations, a common set of orbitals designed to describe a set of electronic states is used in a subsequent CI diagonalization. Such a procedure is relatively efficient and is expected to work well, provided the optimal orbitals for all the states of interest are not very different. However, the strategy used to obtain the state-averaged orbitals involves minimization of an energy functional that weighs the electronic states arbitrarily and is therefore not amenable to a black-box procedure. Furthermore, if there is a significant difference between the best one-electron picture of the electronic states, such a state-averaged scheme cannot work very well because all electronic states will be described poorly. In addition, the size of the configuration space required in these calculations is larger than that needed for state-specific MCSCF calculations, resulting in great computational demands.

The considerations discussed above clearly show that multireference CI approaches to the study of excited states require great care and are not well suited to black-box applications. Ideally, one would like a method that retains the conceptual simplicity of the ΔCI approach while providing a better description of excited states. Since the problems associated with the ΔCI method are due to the use of a single determinant reference state for all electronic states, one might naturally wonder whether a "better" (more flexible) reference state can be used. In other words, we assume the same form of the excited state wavefunction

$$|\Psi_K\rangle = R_K|\Psi_0\rangle \qquad [68]$$

but no longer take $|\Psi_0\rangle$ to be a single determinant. Let us consider the case in which the reference function is the CC wavefunction

$$|\Psi_0\rangle = \exp(T)|\Phi_0\rangle \qquad [69]$$

where $|\Phi_0\rangle$ is the SCF determinant. After inserting this expression into the Schrödinger equation and carrying out a few manipulations similar to the EOM ionization problem, but here for the same number of electrons, and subtracting the ground state solution, one obtains

$$\exp(-T)\hat{H}\exp(T)R_K|\Phi_0\rangle = \Delta E_K R_K|\Phi_0\rangle \qquad [70]$$

or, equivalently,

$$\bar{H}\, R_K|\Phi_0\rangle = \Delta E_K R_K|\Phi_0\rangle \qquad [71]$$

There is a CI-like eigenvalue equation for the excitation energy, ΔE_K, except that the Hamiltonian $(\hat{H})$ has been replaced by $\bar{H}$ and includes the ground state correlation. Again, in practical calculations, the T operator must be truncated to a suitable level of excitation, typically, $T = T_1 + T_2$, which defines the CCSD model for the ground state. Such a reference is much more flexible than that used in ΔCI studies, yet this approach retains the feature of using a common set of orbitals to describe all states. Nevertheless, for finite truncations of T, the excited state wavefunction is more constrained than the ground state CC solution. One therefore expects some residual bias in favor of the ground state. However, the numerical consequences of this imbalance are necessarily smaller than those associated with single reference ΔCI approaches. This equation-of-motion, coupled-cluster (EOM-CC) method, with $T = T_1 + T_2$ and $\hat{R}_k = \hat{R}_{k_1} + \hat{R}_{k_2}$, has recently been implemented into the ACES II program system.[114-116,122] We believe that this method (and its closely related Fock space MR-CCSD)[27-29,123] will eventually become the most commonly used high level approach for the study of excited states. (Unlike the case for ionization potentials and electron affinities, here these two methods do not give exactly the same answers. See also SAC-CI.[124])

Before discussing the numerical accuracy of various methods, some mention should be made of the special demands placed on basis sets in excited state calculations. Superficially, excited states can be grouped into two categories: valence type and Rydberg type. In the former category, the spatial extent of the electronic probability distribution is similar to that in the ground state, whereas Rydberg states have significantly more diffuse electronic wavefunctions. Because of the large difference in the character of the density between the ground and Rydberg-type excited states, basis set considerations are important. To properly describe Rydberg states, one is forced to use basis sets that contain at least a few diffuse functions, which are needed to describe the long-range features of the electronic charge cloud. Usually, Rydberg states are characterized by a hydrogen-atom-like designation ($n = 3$, $n = 4$, etc.) with energies that converge toward some ionization limit. In practice, a few diffuse functions usually provide a good description of the $n = 3$ levels, while more and more diffuse functions are required for accurate calculations of higher levels.

Some commonly used basis sets that contain diffuse functions are the augmented correlation consistent basis sets of Dunning (PVDZ+, PVTZ+, PVQZ+, etc.),[66] the atomic natural orbital basis sets of Widmark, Malmqvist, and Roos (WMR),[64] the polarized basis sets of Sadlej (POL1),[67] and augmented variants of the 6-31G and 6-311G basis sets[125] (6-31G+, 6-31G+(d,p), etc.). (All these basis sets are available in the ACES II program library.) For most routine calculations, we recommend use of the POL1 basis sets, which are relatively small and appear to provide reasonable results for valence transitions as well as the first level of Rydberg states. The amount of Rydberg character is easily monitored by comparing the second moment of the electronic charge distribution $\langle r^2 \rangle$ to that calculated for the ground state. These values can be obtained from the associated one-particle density matrices, which are evaluated in a straightforward way for all the approaches discussed here (TDA, RPA, ΔCI, EOM-CC).[116] For valence states, the standard basis sets usually used to compute energy differences and molecular geometries (6-31G*, DZP, TZ2P, etc.) should be acceptable because the ground and excited state electron densities have similar spatial extent.

The accurate prediction of excitation energies and associated excited state geometries and properties is one of the more challenging areas of quantum chemistry. All the methods that are easily applied to calculating a spectrum of excited states treat the ground state somewhat more completely than the excited states, so improvements in the level of theory usually tend to reduce the predicted excitation energies. Furthermore, for Rydberg-type excited states, basis set improvements also lead to a systematic lowering of the predicted values. Hence, although fortuitous cancellation of basis set and correlation effects is observed in some applications of quantum chemistry (such as the prediction of equilibrium geometries and vibrational frequencies), these effects act in concert in excitation energy calculations.

We now turn to a brief survey of the numerical performance of various methods for singlet–singlet transitions from closed-shell ground states. (The EOM-CC implementation in ACES II is equally applicable to open-shell ground states, but we do not discuss excitation energies of open-shell molecules simply because very little experience has been gained thus far in these calculations.) Furthermore, since all optically allowed (and therefore most interesting) transitions from closed-shell ground states are of the singlet–singlet variety, we also do not consider singlet–triplet transitions. Nevertheless, the accuracy of excitation energies calculated for singlet–triplet processes will always be comparable to that for the corresponding singlet–singlet energy difference. However, these transitions are not allowed by spin and therefore carry no oscillator strength in the nonrelativistic Born–Oppenheimer approximation.

To "factor out" basis set effects, we first compare in Table 24 full configuration interaction (FCI) excitation energies and dipole strengths (the values in parentheses) to those obtained with the TDA, RPA, ΔCISD, and EOM-CCSD approximations. Because FCI is a very expensive method, which has a factorial dependence on the number of electrons, we are restricted to a small system and present comparisons only for the beryllium atom and the CH^+ molecule.[116]

The results in Table 24 clearly illustrate many of the points made in our earlier discussion. For most of the excitations considered here, the ΔCISD results are in the poorest agreement with the FCI excitation energies. All these values are much too large, reflecting the unbalanced nature of the method in favor of the ground state. The RPA and TDA results are in better agreement, with the former providing systematically lower excitation energies than the latter. Nevertheless, none of these three approaches can be said to provide quantitative predictions of the excitation energies.

The EOM-CCSD results, however, are in good agreement with the FCI calculations. Note that there is a clear negative correlation between the quality of the results obtained at this level and the values in the rightmost column under the heading "AEL" (approximate excitation level). These numbers provide a measure of the number of electrons that are "excited" in the transition between the ground and excited states. For excitations that are well described by single excitations (AEL values near 1.0), the EOM-CCSD excitation energies are in excellent agreement with the FCI values. However, larger errors are noted for transitions that have significant double-replacement character. Note also that the TDA and RPA approaches also fail completely for these transitions because they are ultimately one-electron models. The performance of EOM-CCSD for excitations with AEL values much larger than unity is relatively poor because the final state wavefunctions corresponding to these processes are constrained to a greater degree than those for nearly pure single excitations. Better results would be achieved by a more elaborate EOM-CC approach,

Table 24 Comparison of Different Methods for Excitation Energies (eV) and Dipole Strengths (in parentheses, atomic units) with Full CI for States of Be[a] and CH^{+}[b,c]

Final state symmetry	Method					
	TDA	RPA	ΔCISD	EOM-CCSD	FCI	AEL[d]
Be						
^1S	6.13	6.12	7.69	6.77	6.77	1.06
^1S	7.26	7.26	8.97	8.08	8.08	1.04
^1P	5.05 (2.548)	4.80	6.24	5.32 (3.564)	5.32 (3.549)	1.06
^1P	8.77 (0.101)	6.72	8.39	7.47 (0.021)	7.46 (0.022)	1.06
^1D	6.94	6.93	8.03	7.16	7.09	1.59
^1D	7.59	7.59	8.97	8.06	8.03	1.22
CH$^+$						
$^1\Sigma^+$	17.60 (0.102)	17.52 (0.195)	9.92	9.11 (0.025)	8.55 (0.025)	1.96
$^1\Sigma^+$	13.75 (0.986)	13.70 (0.933)	14.94	13.58 (1.073)	13.52 (1.080)	1.06
$^1\Pi$	2.93 (0.097)	2.65 (0.109)	4.46	3.26 (0.095)	3.23 (0.080)	1.03
$^1\Pi$	15.23 (0.585)	14.84 (0.891)	15.57	14.45 (0.692)	14.13 (0.588)	1.24
$^1\Delta$	49.03	49.02	8.44	7.89	6.96	1.98
$^1\Delta$	59.79	59.77	18.49	17.34	16.83	1.66

[a] (9s9p5d) basis.
[b] (14s5p1d) basis.
[c] Reference 116.
[d] Approximate excitation level (see text).

particularly one in which T is approximated by $T_1 + T_2 + T_3$. However, such calculations would scale with the eighth power of the number of basis functions and are not a practical method for routine applications. Approximate inclusion of T_3, as in CCSD(T) or CCSDT-1 should offer some improvement, however. Namely, when an excited state involves significant double excitations, the triple excitation operators (T_3 and R_3) would introduce correlation corrections analogous to those carried by T_2 and R_2 for "single" excitations.

For optically allowed transitions, dipole oscillator strengths predicted by the EOM-CCSD model are superior to those calculated at the RPA and TDA levels and are in relatively good agreement with the FCI results for all the transitions that have AEL values near 1.0. The behavior of the oscillator strengths versus the AEL diagnostic parallels that of the predicted excitation energies, as it should, because both quantities ultimately depend on the quality of the excited state wavefunction. The perfect agreement between the EOM-CCSD and FCI oscillator strengths for the nearly pure $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ double excitation in CH^+ is clearly fortuitous.

In applications of the EOM-CCSD approach to chemical problems, two factors must be carefully considered. As discussed above, the method works best for processes that are well described by single electron transitions, so some degree of caution must be exercised when studying excitations that have a fair amount of double-excitation character (somewhat arbitrarily, we place the cutoff for this "dangerous" region at AEL values of 1.2 and larger). In addition, the basis set used in these calculations must be properly chosen. The latter point is particularly true for the study of Rydberg-like states, where basis sets containing diffuse functions (such as POL1) should be used.

Assume that a DZP basis is used to study excited states of water. If such a calculation is performed, the $\langle r^2 \rangle$ values for the excited states will be similar to the ground state value. This does not mean that the excited states of water are valence type! Indeed, the DZP basis is inherently incapable of describing Rydberg-type states because it does not contain diffuse functions. If a more flexible basis such as POL1 is used, the $\langle r^2 \rangle$ values for the excited state will be much larger than those of the ground state, showing that these are actually Rydberg states. Valence states may be identified as those for which expansion of the basis from a valence set, such as DZP, to a diffuse basis, such as POL1, does not significantly change the calculated values of $\langle r^2 \rangle$. To simplify matters and to make calculations less expensive, it is probably best to carry out TDA calculations with the two different types of basis set and identify the states as either Rydberg or valence. Then, an appropriate basis can be selected for the higher level calculations.

In Table 25 we present results of TDA and EOM-CCSD calculations for the ketene molecule. This system has an extraordinarily complex electronic spectrum, which has been the subject of a number of experimental and theoretical analyses. It also illustrates many features of excited state calculations.

Table 25 Excitation Energies of Ketene (eV) and Corresponding Dipole Oscillator Strengths (in parenthesis, atomic units)

	DZP basis			
Final state	TDA	EOM-CCSD	AEL	Experimental
$^1A_2$	4.38	4.04	1.08	3.84
$^1A_1$	8.63	8.15 (0.156)	1.08	6.78
$^1B_2$	9.64	8.98 (0.0006)	1.07	5.86
2^1A_2	9.97	9.60	1.10	
2^1B_2	10.94	10.34 (0.006)	1.07	
2^1A_1	11.34	10.95 (0.946)	1.09	

	POL1 basis				
Final state	TDA	EOM-CCSD	$\langle r^2 \rangle^a$	AEL	Experimental
$^1A_2$	4.32	3.98	40.18	1.08	3.84
$^1A_1$	7.83	7.22 (0.165)	48.3	1.08	6.78
$^1B_2$	6.41	5.89 (0.033)	48.8	1.07	5.86
2^1A_2	7.52	7.09	55.0	1.06	
2^1B_2	7.73	7.20 (0.008)	57.8	1.07	
2^1A_1	8.54	8.12 (0.033)	47.9	1.07	

[a] Ground state $\langle r^2 \rangle$ value is 41.0 au.

Reliable experimental results for the excitation energies of ketene are limited to the three lowest electronic states, which are believed to be $^1A_2$, $^1A_1$, and $^1B_2$, respectively. If we first look at the results obtained with the DZP basis set, we note that all AEL values are in the range 1.07–1.10, indicating that the EOM-CCSD model probably provides a good treatment of differential electron correlation between the ground and excited states. However, the second and third excitation energies predicted by these calculations are in very poor agreement with the experimental values. In fact, while the experimental value for the $X^1A_1 \rightarrow {}^1B_2$ transition is approximately 1 eV below that for excitation to the $^1A_1$ state, the EOM-CCSD results obtained in the DZP basis predict the opposite behavior, with a splitting of nearly 1 eV favoring the $^1A_1$ state. While it would be tempting to speculate that the errors are systematic and the ordering deduced from the experiments incorrect, it is also well known that Rydberg states are ubiquitous in multiply bonded organic molecules. Hence, before glibly jumping to conclusions, it is always worthwhile to use a larger basis set.

The results (Table 25) obtained with a basis suitable for the study of Rydberg states (the POL1 basis) are strikingly different from those obtained with DZP. Although the lowest energy $X^1A_1 \rightarrow {}^1A_2$ excitation does not change significantly, incorporation of diffuse functions into the basis set lowers some of the other excitation energies by as much as 3 eV! Differences between the excited and ground state $\langle r^2 \rangle$ values are roughly proportional to the energy lowerings brought about by incorporating diffuse functions in the basis set. In particular, note that the ordering of electronic energy levels is now in agreement with experimental assignments. Predicted excitation energies are still a bit on the high side for the first and third transitions. Nearly perfect agreement is achieved for the $X^1A_1 \rightarrow {}^1B_2$ transition, with the EOM-CCSD result a mere 0.03 eV above the experimental value. It is significant to note that this is the most well-established experimental result in Table 25 and corresponds to a vertical excitation energy. The experimental values for excitation to the first and third levels are less certain and probably correspond more closely to adiabatic (equilibrium geometry to equilibrium geometry) than vertical excitation processes. This is another feature that must be carefully considered in studying excited states, since excitation energies obtained from experiment often are affected by changes in equilibrium geometries between the two states. Since the equilibrium geometry of the excited state is necessarily lower in energy than that associated with the vertical transition, adiabatic transition energies will always be lower than the vertical values.

In addition, all the ketene states discussed above are open-shell singlets, which require at least two determinants in a zeroth-order description as discussed earlier. An approach for an in-depth study specific to one of these states is offered by the two-determinant, TD-CCSD, multireference method.[31] In ketene, with a DZP basis the TD-CCSD vertical excitation energy is 3.83 for the ${}^1A_2$ state in excellent agreement with experiment, while the 2^1A_1 state is at 8.64 eV compared to the EOM-CCSD value of 8.15 eV. For the same two states, the Fock space MR-CCSD gives 3.83 and 7.89 eV. Other methods related to EOM-CC include polarization propagator (PP) procedures[38] built on a second order [MBPT(2)] ground state wavefunction (e.g., the SOPPA method) and more general methods of analysis that use a CC ground state reference (e.g., CCPPA).

It is hoped that this section provides a useful introduction to ab initio studies of excited states. In this challenging area in quantum chemistry, it is not always straightforward to compare results of such calculations with experimental values because information about molecular excited states (and, in particular, the associated potential energy surfaces) is very scarce. Indeed, while the prediction of infrared spectra has clearly been the most fruitful area of application for quantum chemical methods in the past decade, it is likely that theoretical studies of electronically excited states will continue to grow in importance. In particular, the availability of accurate (and therefore predictive) methods such as the EOM-CCSD approach in programs such as ACES II will serve to make accurate calculations of these systems accessible to a wide range of users.

MOLECULAR PROPERTIES

First-Order Properties

Properties of interest can be static or dynamic (i.e., time or frequency dependent); first, second, or higher order; and one- or two-particle type. First-order static one-electron properties (dipole and quadrupole moments, electric field gradients, hyperfine coupling constants, etc.) are obtained by integrating over the molecular charge density.[126] That is, for some one-particle operator $\hat{\theta} = \Sigma_i \hat{\theta}(i)$ [e.g., for a dipole moment in atomic units $\hat{\theta} = \Sigma_i \mathbf{r}(i)$],

$$\langle \hat{\theta} \rangle = \int \Psi^*(12 \ldots n) \sum_i \hat{\theta}(i) \Psi(12 \ldots n) d\tau \qquad [72]$$

$$\langle \hat{\theta} \rangle = \int \hat{\theta}(1) \rho(1) d\tau \qquad [73]$$

where

$$\rho(1) = \int \Psi(12 \ldots n) \Psi^*(12 \ldots n) d\tau_2 d\tau_3 \ldots d\tau_n \qquad [74]$$

and $\rho(1)$ is the (spin-dependent) molecular charge density.

Another, more general way to define a property is via perturbation theory, where the usual electronic Hamiltonian, H (now $H(0)$) has a perturbation $\lambda\hat{\theta}$ added to it. (The "0" argument of H should be taken to mean that the Hamiltonian does not contain the perturbation of interest. It should not be confused with a Hamiltonian that ignores electron correlation.) Then

$$\mathcal{H} = H(0) + \lambda\hat{\theta} = H(0) + \lambda \frac{\partial \mathcal{H}}{\partial \lambda} \qquad [75]$$

and the Schrödinger equation for the perturbed Hamiltonian gives us

$$\mathcal{H}\Psi(\lambda) = E(\lambda)\Psi(\lambda) \qquad [76]$$

Then, expanding $\Psi(\lambda)$ and $E(\lambda)$ in a Taylor series,

$$\Psi(\lambda) = \Psi(0) + \frac{\partial \Psi}{\partial \lambda} \lambda + \frac{1}{2} \frac{\partial^2 \Psi}{\partial \lambda^2} \lambda^2 + \cdots \qquad [77]$$

$$E(\lambda) = E(0) + \frac{\partial E}{\partial \lambda} \lambda + \frac{1}{2} \frac{\partial^2 E}{\partial \lambda^2} \lambda^2 + \cdots \qquad [78]$$

Inserting Eqs. [77] and [78] into Eq. [76], and insisting that the coefficient of each power of λ be the same on both sides of the equation, we have

$$\frac{\partial E}{\partial \lambda} = \langle \Psi(0) | \theta | \Psi(0) \rangle + 2 \left\langle \frac{\partial \Psi}{\partial \lambda} | H(0) - E(0) | \Psi(0) \right\rangle \qquad [79]$$

Provided we know the solution to the unperturbed Schrödinger equation

$$H(0)\Psi(0) = E(0)\Psi(0) \qquad [80]$$

$$\frac{\partial E}{\partial \lambda} = \left\langle \Psi(0) \middle| \frac{\partial \mathcal{H}}{\partial \lambda} \middle| \Psi(0) \right\rangle = \langle \Psi(0)|\hat{\theta}|\Psi(0)\rangle = \langle \hat{\theta} \rangle \qquad [81]$$

there is an exact equivalence between the first derivative and the expectation value. The fact that we obtain the property from the first derivative of E, the first term in the power series, justifies the terminology "first-order" property. In the next section we will consider second-order properties.

Equation [81] is a statement of the Hellmann–Feynman theorem, which always holds when we have the exact solution for the unperturbed Schrödinger equation (Eq. [80]). However, the Hellmann–Feynman theorem is true only for certain classes of approximate wavefunctions. Except for energy derivatives as previously discussed, where the Gaussian basis is fixed to the nuclear centers in a molecule and therefore changes when the nuclei are displaced, basis functions are usually independent of the perturbation $\lambda\hat{\theta}$. (An exception occurs when field-dependent or gauge-including orbitals are employed, as in NMR and magnetic susceptibility calculations.) This causes the simple Hellmann–Feynman theorem, Eq. [81], to be satisfied for an SCF wavefunction. This follows because it may be shown that any wavefunction that is variationally optimum with respect to variation of all adjustable parameters satisfies the Hellmann–Feynman theorem. In MCSCF, both the MOs and CI coefficients are optimized, so it, too, satisfies Eq. [81] for ordinary properties. However, for CI wavefunctions, the configuration coefficients are variationally optimum but the MOs are not. Similarly, in MBPT or CC theory neither the configuration coefficients nor the MOs are optimum. For the latter cases, the second term in Eq. [79] has a role to play in the accurate treatment of properties and should be included.

In the SCF independent particle case, $\Psi(0) = \Phi_0$, and Eq. [74] becomes

$$\rho(1) = \sum_{i=1}^{n} \varphi_i(1)\varphi_i^*(1) \qquad [82]$$

so

$$\langle \hat{\theta} \rangle = \sum_{i=1}^{n} \langle \varphi_i|\hat{\theta}|\varphi_i\rangle = \mathrm{Tr}(\theta\rho) \qquad [83]$$

The SCF solution for a first-order, one-electron property is usually argued to be relatively accurate. The reason follows from the Møller–Plesset theorem.[4] Earlier we found that the first correlation correction to Φ_0 comes solely from double excitations, $\Phi_0 + \Phi^{(1)} = \Phi_0 + \Sigma_{\substack{i>j\\a>b}} \Phi_{ij}^{ab} C_{ij}^{ab}$. However, $\langle \Phi_0|\theta|\Phi_{ij}^{ab}\rangle = 0$

Table 26 Variation of Ground State Dipole Moments (au) of Selected Small Molecules with Different Basis Sets at the SCF Level[a]

Basis set	OC	H_2O	H_3N	H_2S	HF
STO-3G	0.0661	0.6791	0.7028	0.4026	0.5069
3-21G	−0.1552	0.9581	0.8552	0.7148	0.8479
6-31G	−0.2209	1.0349	0.9139	0.7315	0.9032
6-31G*	−0.1309	0.9595	0.7435	0.5418	0.7759
DZP	−0.0966	0.8604	0.7217	0.5025	0.8065
TZP	−0.1179	0.8671	0.7414	—	0.8063
POL1	−0.0989	0.7804	0.6366	0.4375	0.7566
Experimental	+0.044	0.721	0.578	0.401	0.708

[a] Dipole is positive with A^+B^- polarity.

for a one-electron property, so the quantity $\langle\hat{\theta}| = \langle\Phi_0 + \Phi^{(1)}|\hat{\theta}|\Phi_0 + \Phi^{(1)}\rangle = \langle\Phi_0|\hat{\theta}|\Phi_0\rangle + \langle\Phi^{(1)}|\hat{\theta}|\Phi^{(1)}\rangle$. Hence, all first-order correlation corrections to $\langle\hat{\theta}\rangle$ vanish for an SCF solution because the second term is second order in correlation. Tables 26, 27, and 28 show how well this works in practice for dipole moments, quadrupole moments, and field gradients. As is well known, the SCF dipole moment of CO has the wrong sign. Nevertheless, in the POL1 basis, which is good for such properties, SCF dipoles fall within about 10% of experiment.

When making comparisons to experimental properties, we must emphasize the role of the Gaussian basis set. Ab initio methods obtain answers that are only as reliable as the basis permits. A basis that is good for energy calculations is not usually appropriate without extension for other properties. This is easy to understand. The energy preferentially samples regions of space close to the nuclei via operators like $1/r$ while a dipole moment requires a description of $\hat{r}$ and a quadrupole moment $\hat{r}^2$. The latter are much more sensitive to the diffuse parts of the electronic density. A field gradient depends on the operator $\theta = \Sigma_i\,(3z_i^2 - r_i^2)/r_i^5$, so its $\sim 1/r^3$ dependence makes it particularly sensitive to regions of the density near the nucleus. Hyperfine coupling constants are derived from spin densities—that is, $A_{\text{iso}} = (8\pi/3h)g_e g_N \mu_e \mu_N[\rho^\alpha(0) - \rho^\beta(0)]$—and therefore depend on the density exactly at the nucleus. Hence, to describe

Table 27 Variation of Electric Quadrupole Moment (au) of Selected Small Molecules with Different Basis Sets at the SCF Level

Basis set	CO	H_2O	NH_3	H_2S	CO_2	HF
STO-3G	−2.2512	0.0081	0.5977	0.2329	−3.9096	0.9230
3-21G	−2.1529	−0.0622	0.8687	0.5148	−5.2684	1.5054
6-31G	−2.1331	−0.1213	0.9928	0.5416	−5.4341	1.5748
6-31G*	−1.6117	−0.1292	0.9558	0.6905	−4.0916	1.6525
DZP	−1.6494	−0.1043	1.0240	0.6755	−4.0932	1.6798
TZP	−1.7010	−0.1194	1.0920	—	−4.2469	1.7040
POL1	−1.5368	−0.0989	1.0637	0.7883	−3.8087	1.7426

Table 28 Variation of Electric Field Gradient (au) at Atomic Centers of Selected Small Molecules with Different Basis Sets at the SCF Level

Molecule	Center	STO-3G	3-21G	6-31G	6-31G*	DZP	TZP	POL1
CO	O	0.0683	−0.5323	−0.4268	−0.4674	−0.4371	−0.6813	−0.4812
	C	−0.4424	−0.8047	−0.8926	−0.9936	−0.9809	−1.0964	−1.0600
CO_2	O	1.3985	0.8574	1.0481	0.8633	0.9406	0.7776	0.8866
	C	0.1694	−0.3780	−0.4528	−0.5846	−0.5463	−0.6566	−0.6417
HF	H	0.5785	0.7165	0.6315	0.5704	0.5697	0.5784	0.5777
	F	3.8582	3.1783	3.1311	2.9803	2.9714	2.9168	2.8766
H_2S	S	1.2287	0.5398	0.5335	0.4021	0.4508	—	0.3580
	H	0.0609	0.0663	0.0657	0.0608	0.0630	—	0.0712
H_2O	O	0.3146	0.2267	0.2440	0.2116	0.2217	0.1877	0.2205
	H	0.0220	0.0298	0.0196	0.0239	0.0407	0.0388	0.0418
NH_3	N	0.7957	0.5361	0.5147	0.4844	0.4942	0.4899	0.4781
	H	0.2165	0.2341	0.2265	0.1990	0.2100	0.2098	0.2131

all the above equitably requires basis sets augmented in both the core and diffuse regions. Such simultaneous extensions are seldom practical, so different basis sets tailored to different properties are usually used in practice.

As we have seen in Tables 26–28, the nature of the basis set has a dramatic effect on a property at the SCF level, so that aspect needs to be under control[127] before we can reliably assess the role of electron correlation. Finally, we should also note that whereas the energy is variational and the wavefunction can be optimized to give the lowest energy, the same cannot be done for other properties (there are some useful bounds that pertain to second-order properties, however). As a result, we can never be certain that properties obtained at increasingly more complete levels of theory will systematically converge to the exact result.

Using the perturbation theory approach to properties, we can always evaluate a property by simply adding $\lambda\hat{\theta}$ to the electrostatic Hamiltonian, for some small value of λ, and solve directly for the $E(\lambda)$ in Eq. [76]. (Variants of the finite field procedure include placing the molecule in a field generated by point charges a long distance away rather than explicitly adding the finite field to the Hamiltonian as described above.) By repeating for the same small value of λ but with a negative sign, we obtain $E(-\lambda)$. Inasmuch as our objective is $\partial E/\partial\lambda$, we know

$$\frac{\partial E}{\partial \lambda} \approx \frac{E(\lambda) - E(-\lambda)}{2\lambda} \qquad [84]$$

and in the limit of $\lambda \to 0$, we obtain the exact derivative. Since each $E(\lambda)$ calculation would routinely be done by reoptimizing the MOs in the presence of the perturbation and, in the case of a correlated calculation, the configuration coefficients, in this procedure we are actually including the effects of the non-Hellmann–Feynman terms in Eq. [79]. Even though this approach seems to make good sense only for properties such as dipole moments, where $\lambda\theta = \Sigma_i \boldsymbol{\epsilon} \cdot \mathbf{r}_i$ and we can "turn on" the electric field strength vector $\boldsymbol{\epsilon}$, we can actually evaluate any first-order property in this way. For example, the spin density is not usually thought to be a field-dependent property, but we can add an operator to H and evaluate spin densities.[128] Hence, this "finite field" procedure is simply an artifice for indirectly calculating the property.

In finite field calculations we have to worry about numerical accuracy because the field strength must be large enough to cause an adequate change in the significant digits of $E(\lambda)$, but should also be small enough to make the numerical derivative accurate. Typically fields of 0.001 to 0.005 au are used for dipole moments and polarizabilities, but for the hyperpolarizabilities β and γ, which are third and fourth derivatives of the energy with respect to an electric field, the precision of finite-field calculations can be questioned. A field strength of $(0.001)^4 = 10^{-12}$ means that more than 12 significant digits in the energy are necessary to evaluate γ accurately. This is typically beyond the precision of the molecular integral evaluation. Finally, of formal but generally not numerical significance, adding an electric field to the electrostatic Hamiltonian gives an $\mathcal{H}(\lambda)$ that is unbound. Its exact solution corresponds to the experimentally well-known field ionization, leading to a cation plus an electron. The use of a finite basis set makes the field-ionized solution, which requires a continuum description of the free electron, inaccessible, so practical finite field calculations should not run into this difficulty.

The solution to all the foregoing reservations lies in analytical evaluation of first-order properties. The critical quantity is the "relaxed" density[84,129] $D(1) = \Sigma_{p,q}\ \varphi_p(1)D_{pq}\varphi_q^*(1)$ when D_{pq} consists of the one-particle response density and the MO relaxation part. This is the same density used in analytical gradients, but the final form of the equations for ordinary properties is just $\langle\hat{\theta}\rangle = \int\hat{\theta}(1)D(1)d\tau = \Sigma_{p,q}\ \hat{\theta}_{pq}D_{pq}$. The finite field procedure is clearly less desirable than a calculation based on "relaxed density" because once $D(1)$ has been obtained, all one-electron properties can be rapidly evaluated by just multiplying D_{pq} with the appropriate integral θ_{pq} and summing. Alternatively, many separate finite field calculations would be needed to get all properties. We will thus have a D_{pq} for all levels of theory where analytical gradients have been implemented (MBPT(2), MBPT(3), MBPT(4), CCSD, CCSD(T), QCISD(T), etc.) in ACES II. With the aid of this quantity, we can investigate the role of electron correlation on molecular properties.

Results for dipole moments are shown in Table 29.[130] Clearly, coupled with good basis sets, correlated methods can do quite well for this property. Elsewhere, we have used relaxed density-based CC and MBPT methods to study spin densities[129] and the related hyperfine coupling constants; to evaluate relativistic corrections (Darwin and mass–velocity term) when important;[131] and to evaluate highly accurate electric field gradients to extract nuclear quadruple moments.[132]

Table 29 Variation of Ground State Dipole Moments (au) of Selected Small Molecules with Different Basis Sets and Correlated Methods

Basis set	OC	H_2O	H_3N	H_2S	HF
DZP-MBPT(2)	0.1447	0.8229	0.7102	0.4902	0.7642
DZP-CCSD	0.0585	0.8163	0.6990	0.4626	0.7602
DZP-CCSD(T)	0.0752	0.8114	0.6963	0.4599	0.7564
TZP-MBPT(2)	0.1222	0.8387	0.7368	—	0.7671
TZP-CCSD	0.0344	0.8294	0.7249	—	0.7625
TZP-CCSD(T)	0.0558	0.8248	0.7229	—	0.7580
POL1-MBPT(2)	0.1208	0.7297	0.5994	0.4053	0.7079
POL1-CCSD	0.0421	0.7287	0.5975	0.3924	0.7079
POL1-CCSD(T)	0.0581	0.7215	0.5904	0.3857	0.7014
Experimental	+0.044	0.721	0.578	0.401	0.708

Second-Order Properties

Second order properties derive from the second derivative term in Eq. [78]. For the most general case we should also allow for a second-order perturbation, $\mathcal{H}(\lambda) = H(0) + (\partial\mathcal{H}/\partial\lambda)\lambda + ^1\!/_2\,(\partial^2\mathcal{H}/\partial\lambda^2)\lambda^2$ from which differentiation of the Schrödinger equation gives

$$\begin{aligned}\frac{\partial^2 E}{\partial\lambda^2} &= \left\langle \Psi(0)\middle| \frac{\partial^2\mathcal{H}}{\partial\lambda^2} \middle|\Psi(0) \right\rangle \\ &+ 2\left\langle \frac{\partial\Psi(0)}{\partial\lambda} \middle| \frac{\partial\mathcal{H}}{\partial\lambda} - \frac{\partial E}{\partial\lambda} \middle| \Psi(0) \right\rangle \\ &+ 2\left\langle \frac{\partial^2\Psi}{\partial\lambda^2} \middle| H(0) - E(0) \middle| \Psi(0) \right\rangle\end{aligned} \qquad [85]$$

[Allowing λ to be a vector would define all nine components of the second derivative tensor $(\partial^2 E/\partial\lambda_i\partial\lambda_j)$.] For the polarizability tensor where $\lambda\theta = \Sigma_i \boldsymbol{\epsilon} \cdot \mathbf{r}_i$ and many other examples, there is no $\partial^2\mathcal{H}/\partial\lambda^2$ perturbation. Once again, if we cannot solve Eq. [80] exactly (or have all parameters optimum), a non-Hellmann–Feynman term that depends on the second derivative (i.e., second order) perturbed wavefunction must be considered. When the theorem is satisfied, the new information we require is only the first-order perturbed wavefunction, $\partial\Psi/\partial\lambda$. This quantity is equivalent to $\psi^{(1)}$ in Eq. [29b], when $V = \partial\mathcal{H}/\partial\lambda$ and $E^{(1)} = \partial E/\partial\lambda$. We can solve for $\partial\Psi/\partial\lambda$ in the same way as before, by the textbook expedient of expanding in the complete set of solutions to $H(0)$, which means all the excited electronic states, which as eigenfunctions of $H(0)$, are orthogonal to the ground state. Using the zz component of the polarizability as an example,

$$\alpha_{zz} = -2 \sum_{k\neq 0}^{\infty} |\langle\Psi_0|z|\Psi_k\rangle|^2 \,/\, (E_0 - E_k) \qquad [86]$$

Equation [86] is sometimes useful, e.g., when a knowledge of the excitation energies and polarized components of the transition moments for a few states could be used to estimate the α tensor from experiment. However, this sum-over-states formula is computationally about the worst approach to the theoretical evaluation of second-order quantities. To use it directly would require computing all the excited states the finite basis permits and the appropriate transition moments. It can be solved indirectly, however.[133]

The superior approach is to simply compute the second derivative (Hessian) matrix analytically.[134] Just as for force constants, this is the most accurate and efficient procedure when the second-derivative formulas have been programmed. Furthermore, any residual dependence on $\partial^2\Psi/\partial\lambda^2$ is alleviated, just

Table 30 Dipole Polarizabilities (au) for Molecules (POL1 Basis)[a]

	CO_2		N_2		C_2H_4		CO	
	$\bar{\alpha}$[b]	$\Delta\alpha$[c]	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$
SCF	15.8	12.1	11.4	5.4	28.0	12.6	12.2	3.4
MBPT(2)	17.9	15.0	11.5	4.4	27.4	10.2	13.1	3.9
CCSD	17.4	14.4	11.6	4.8	26.9	10.7	12.9	4.0
CCSD(T)	17.6	14.5	11.8	4.9	27.1	10.5	13.0	3.9
Experimental	17.5	13.8	11.8	4.7	28.7	11.0	31.1	3.7

	HF		H_2O		NH_3		H_2S	
	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$	$\bar{\alpha}$	$\Delta\alpha$
SCF	4.9	1.3	8.5	1.1	12.9	0.5	23.6	0.4
MBPT(2)	5.7	1.1	9.8	0.4	14.4	1.9	24.5	0.9
CCSD	5.6	1.2	9.6	0.6	14.1	1.7	24.3	0.9
Experimental	5.5	1.3	9.8	0.6	14.6	1.9	25.5	

[a] Reference 130.

[b] $\bar{\alpha} = 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) = 1/3\ \mathrm{Tr}(\boldsymbol{\alpha})$.

[c] $\Delta\alpha = 1/\sqrt{2}\ [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]^{1/2}$.

as in the gradient case, by introducing the configuration response (via Λ) and the molecular orbital relaxation contribution. [This can be done for open (UHF[92] and ROHF[93]) and closed shells at the MBPT(2) level in ACES II.] To obtain polarizabilities at higher correlated levels, the dipole moment is computed as a function of a finite field $\mu(\boldsymbol{\lambda})$, from which numerical differentiation provides the tensor $\boldsymbol{\alpha}$. Similarly, a second numerical differentiation gives $\boldsymbol{\beta}$ and a third, $\boldsymbol{\gamma}$.[130] The accuracy for $\boldsymbol{\alpha}$ at several levels of theory is shown in Table 30.

NUCLEAR MAGNETIC RESONANCE

Although evaluations of harmonic force constants $(\partial^2 E/\partial q_i \partial q_j)$, electric polarizabilities $(\partial^2 E/\partial \epsilon_i \partial \epsilon_j)$, and dipole moment derivatives $(\partial^2 E/\partial \epsilon_i \partial q_j)$ are perhaps the most common applications of second-order properties (or, equivalently, second derivatives), other areas of interest to chemists can be treated with these techniques. One such field of application that holds great promise for the future is the calculation of nuclear magnetic resonance chemical shifts.

The theoretical study of NMR shifts has a relatively long history. Calculations of magnetic properties inherently suffer from a "gauge origin" problem, which simply means that the results depend on the choice of origin of the coordinate system (e.g., the calculated NMR shifts for water will change if the molecule is "translated" along an axis). This clearly unphysical behavior can be avoided by assigning a local gauge origin to each basis function, which is known as a "gauge-including atomic orbital" (GIAO).[135] This approach was first tried nearly 20 years ago, but a straightforward implementation requires evaluation of difficult integrals, which involve complex quantities, and did not find wide acceptance. Subsequently, a number of methods designed to minimize the gauge origin problem were suggested—the IGLO[136] and LORG[137] techniques—but these still do not completely do away with the problem. Eventually, it was realized that analytic second-derivative techniques could be used to avoid many of the complicated steps involving the GIAO basis function integrals, and a number of applications of the GIAO approach were carried out at the SCF level.[138] In particular, when the second derivatives are evaluated analytically, no arithmetic involving complex numbers needs to be performed.

Elements of the chemical shift tensor σ for a particular nucleus η are given by the mixed second derivative of the energy with respect to the nuclear magnetic moments [$I_{q_i}(\eta)$] and the magnetic field [B_j]

$$\sigma_{ij} = \frac{\partial^2 E}{\partial I_{q_i} \partial B_{q_j}} \qquad [87]$$

The chemical shift is then given by $\frac{1}{3} Tr(\sigma)$.

Applications of the GIAO approach at the SCF level are now relatively routine, but correlated calculations are more difficult because the most convenient implementations of this approach require the analytic evaluation of the second derivatives. Therefore, correlated studies using GIAO basis functions are effectively limited to levels of theory for which analytic second-derivative methods are available. Although the number of calculations thus far carried out on chemical shifts is far too small to give us a clear picture of basis set and correlation effects, the initial results of GIAO-MBPT(2) calculations[139] suggest that correlation is indeed important for these phenomena. In Table 31 are results from a few representative calculations of ^{17}O chemical shifts.

From these results and a limited number of other studies, it appears that the correlation effects are most pronounced for systems with multiple bonds, which should come as no surprise. In addition, it appears that basis set and correlation effects tend to act in different directions, which, of course, can lead

Table 31 ^{17}O Chemical Shifts

Molecule	Basis set	SCF	MBPT(2)	Experimental
H_2O	DZP	331.7	345.4	344.0
	TZ2P	323.2	339.8	344.0
CO_2	DZP	216.9	253.0	243.4
	TZ2P	200.4	236.4	243.4
CO	DZP	−96.7	−27.3	−42.3
	TZ2P	−113.5	−54.1	−42.3

to fortuitous cancellation and the appearance of Pauling points. However, since the GIAO method is currently limited to the SCF and MBPT(2) levels, the effect of higher order correlation corrections on the calculated chemical shifts are not yet known.

ACKNOWLEDGMENTS

Many other members of our research group have significantly contributed to this chapter. All the CASSCF-CI calculations were performed by Dr. Peter Szalay using the COLUMBUS program system. Dr. John Watts provided the CCSDT results for the N_2 curve among several other calculations. Dr. Stanislaw Kucharski provided the CISDT and CISDTQ results. Dr. Anna Balkova is responsible for the TD-CCSD results. Mr. Steve Gwaltney computed some of the vibrational frequencies. Ms. Suely Meth did the MgF^+ calculation. Mr. Ajith Perera computed the first-order properties. Dr. Hideo Sekino did the polarizability calculations. Dr. Jürgen Gauss is responsible for the NMR results. Mr. Sullivan Beck, Mr. Dave Bernholdt, and Dr. Don Comeau offered invaluable help with computer graphics. Finally, Mrs. Sue Linsley typed this long chapter, despite extensive, illegible revisions from the authors. This work has been supported by the Air Force Office of Scientific Research and the Office of Naval Research. We acknowledge the Florida Supercomputer Center and the Ohio Supercomputer Center for their generous allocation of computer resources.

APPENDIX

Quadratic Configuration Interaction (QCI)

What is QCI? To answer this question we need to consider the relationship between CI and CC theory in a little more detail. Since the exact CI wavefunction is $\Psi_{CI} = (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \cdots + \hat{C}_n)\Phi_0$ and $\Psi_{CC} = \exp(\hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n)\Phi_0$, it follows that $\hat{C}_1 = \hat{T}_1$, $\hat{C}_2 = \hat{T}_2 + \hat{T}_1^2/2$, $\hat{C}_3 = \hat{T}_3 + \hat{T}_1\hat{T}_2 + \hat{T}_1^3/3!$ and $\hat{C}_4 = \hat{T}_4 + \hat{T}_2^2/2 + \hat{T}_1^2\hat{T}_2/2 + \hat{T}_1\hat{T}_3 + \hat{T}_1^4/4!$ etc. The inclusion of $\hat{T}_2^2/2$ in even the simplest CCD model explains why CCD is usually better than CID, CISD, or even CISDT. Once we have CISDTQ, this term is picked up along with several others showing that CISDTQ $\simeq$ CCSD(T) (e.g., as shown in Table 4). In operator form, the CISD equations in the canonical SCF case are

$$\langle \Phi_i^a | H_N(\hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle = \Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle$$

$$\langle \Phi_{ij}^{ab} | H_N(1 + \hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle = \Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle$$

$$\Delta E = \langle \Phi_0 | H_N \hat{C}_2 | \Phi_0 \rangle$$

In contrast, in terms of $\hat{C}_p$, the CCSD equations are

$$\langle \Phi_i^a | H_N (\hat{C}_1 + \hat{C}_2 + \hat{C}_3') | \Phi_0 \rangle = \Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle \qquad [88]$$

$$\langle \Phi_{ij}^{ab} | H_N (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3' + \hat{C}_4') | \Phi_0 \rangle = \Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle \qquad [89]$$

$$\Delta E = \langle \Phi_0 | H_N \hat{C}_2 | \Phi_0 \rangle$$

where $\hat{C}_3' = C_3 - T_3$ and $\hat{C}_4' = C_4 - \hat{T}_4 - \hat{T}_1\hat{T}_3$. Remember, while the ΔE remains in CI, it has to disappear from extensive methods. Algebraic analysis shows that $\Delta E \langle \Phi_i^a | \hat{C}_1 | \Phi_0 \rangle$ (which is an unlinked term) is equal to a term derived from $\hat{T}_1\hat{T}_2$ in C_3' in Eq. [88]. Similarly, $\Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle$ equals a term arising from the $\hat{T}_2^2/2 + \hat{T}_1^2\hat{T}_2/2$ terms in C_4' in Eq. [89]. Eliminating the corresponding terms from the equations eliminates ΔE, making the CCSD method extensive.

The idea of QCI is to replace these essential terms by the closest CI coefficient analog. Namely, $\hat{C}_1\hat{C}_2 = \hat{T}_1\hat{T}_2 + \hat{T}_1^3/2$ and $\hat{C}_2^2/2 = \hat{T}_2^2/2 + \hat{T}_1^2 T_2/2 + \hat{T}_1^4/4$. Hence, the QCISD equations are

$$\langle \Phi_i^a | H_N (\hat{C}_1 + \hat{C}_2 + \hat{C}_1\hat{C}_2) | \Phi_0 \rangle = \Delta E \langle \Phi_i^a | \hat{C}_1 | \phi_0 \rangle$$

$$\left\langle \Phi_{ij}^{ab} | H_N \left(1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_2^2/2\right) | \Phi_0 \right\rangle = \Delta E \langle \Phi_{ij}^{ab} | \hat{C}_2 | \Phi_0 \rangle \qquad [90]$$

$$\Delta E = \langle \Phi_0 | H_N \hat{C}_2 | \Phi_0 \rangle$$

These differ from CCSD via the C_3' term in the double-excitation equation and the different numerical factors in the $\hat{T}_1^3$ and $\hat{T}_1^4$ terms, but none of these terms is required to cancel unlinked terms. Also, none of these terms contributes before the fifth-order energy in the canonical SCF case. So usually QCISD $\simeq$ CCSD (see Table 32). QCISD's mean error of 6.41 compares with 7.06 for CCSD. Also, since nonlinear T terms tend to raise the correlation energy, their neglect in QCISD will usually cause $E(\text{QCISD}) < E(\text{CCSD})$ slightly. If we restrict ourselves to just CCD, then QCID = CCD. Also, it is apparent from the derivation above that QCISD is an extensive (i.e., many-body) method. It is also clear that for two electrons, CISD = QCISD = CCSD. Unlike CCSD, QCISD is defined only in the canonical SCF case. Besides keeping the effects of $\hat{T}_1$ small because of the Brillouin theorem, this is necessary to maintain the extensive property of the method: otherwise, $\Delta E = \langle \Phi_0 | H_N (\hat{C}_1 + \hat{C}_2) | \Phi_0 \rangle$ and adding the additional C_1C_2 term to Eq. [90] and $\hat{C}_1^2/2$ in the single excitation equation can lead to residual unlinked terms in the wavefunction. This is also why there is no extensive QCISDT method.[140]

Noniterative T_3 contributions can be added to QCISD just as in the CCSD case. The contribution from double excitations to T_3 is formally exactly the same T(CCSD) term, except that it is evaluated using QCISD coefficients, that is, T(QCISD). QCISD(T) further adds a single excitation term like CCSD(T), but it needs to be multiplied by 2 compared to CCSD because the C_3' term remaining in Eq. [89] introduces this term once and iteratively in CCSD.

Table 32 Differences (millihartrees) Between QCI and Full CI Energies (DZP Basis Set)

Method	BH			FH			H_2O			Mean absolute error
	R_e	1.5 R_e	2.0 R_e	R_e	1.5 R_e	2.0 R_e	R_e	1.5 R_e	2.0 R_e	
QCISD	1.75	2.35	3.84	2.57	4.14	8.40	3.88	9.37	21.38	6.41
QCISD(T)	0.40	0.41	0.12	0.24	0.66	1.38	0.62	1.81	−1.26	0.77
QCISD(TQ*)[a]	0.05	−0.09	−0.85	0.17	0.34	0.87	0.09	−0.13	−1.08	0.41

[a] QCISD(TQ*) = QCISD + TQ*(QCISD) from reference 49.

Unlike CI, where $\Psi_{\text{CISD}} = (1 + \hat{C}_1 + \hat{C}_2)\Phi_0$, and CCSD, where $\Psi_{\text{CCSD}} = \exp(\hat{T}_1 + \hat{T}_2)\Phi_0$, the Ψ_{QCISD} wavefunction cannot be simply represented. It is an approximate truncation of $\exp(\hat{T}_1 + \hat{T}_2)\Phi_0$ that is *different for the single and double excitation projections.* The QCISD(T) mean error of 0.77 compares to 1.15 for CCSD(T). Also adding T_4 effects gives QCISD(TQ*), whose mean error of 0.41 is close to that of CC5SD(TQ*), 0.44. QCISD and QCISD(T) are simply approximate versions of the CCSD and CCSD(T) equations; therefore all the analytical gradient and other methods in ACES II contain QCI as a special case.

REFERENCES

1. This chapter presents the kind of information communicated to participants of workshops on applied molecular orbital theory and to new graduate students. The choice of topics is based on our experience with these groups.
2. D. B. Boyd, in *Reviews in Computational Chemistry,* Vol. 4, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1993, pp. 229–257. Compendium of Software for Molecular Modeling.
3. J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett, *Int. J. Quantum Chem.,* **S26,** 879 (1992). The ACES II Program System.
4. A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry,* Macmillan, New York, 1990.
5. R. J. Bartlett, *Annu. Rev. Phys. Chem.,* **32,** 359 (1981). Many-Body Perturbation Theory and Coupled Cluster Theory for Electron Correlation in Molecules.
6. R. J. Bartlett, *J. Phys. Chem.,* **93,** 1697 (1989). Coupled-Cluster Approach to Molecular Structure and Spectra: A Step Toward Predictive Quantum Chemistry.
7. P. Carsky and M. Urban, *Ab Initio Calculations,* Springer-Verlag, Berlin, 1980.
8. W. J. Hehre, J. A. Pople, P. v. R. Schleyer, and L. Radom, *Ab Initio Molecular Orbital Theory,* Wiley, New York, 1986. (This book offers a wealth of comparisons of SCF results and those from perturbation theory in a variety of basis sets.)
9. I. Shavitt, in *Methods of Electronic Structure Theory,* H. F. Schaefer, III, Ed., Plenum, New York, 1977, p. 189. The Method of Configuration Interaction.
10. F. W. Bobrowicz and W. A. Goddard, III, in *Modern Theoretical Chemistry III,* H. F. Schaefer, III, Ed., Plenum, New York, 1977, p. 79. The Self-Consistent Field Equations for Generalized Valence Bond and Open-Shell Hartree–Fock.
11. J. Čížek and J. Paldus, *Physica Scripta,* **21,** 251 (1980). Coupled-Cluster Approach.
12. R. J. Bartlett, C. E. Dykstra, and J. Paldus, in *Advanced Theories and Computational Approaches to the Electronic Structure of Molecules,* C. E. Dykstra, Ed., Reidel, Dordrecht, 1984, p. 127. Coupled-Cluster Methods for Molecular Calculations.
13. J. A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.,* **87,** 5968 (1987). Quadratic Configuration Interaction. A General Technique for Determining Electron Correlation Energies.
14. B. O. Roos, *Adv. Chem. Phys.,* **69,** 399 (1987). The Complete Active Space Self-Consistent Field Method and Its Application in Electronic Structure Calculations.
15. I. N. Levine, *Quantum Chemistry,* Prentice-Hall, Englewood Cliffs, NJ, 1991 (especially Chapters 15 and 17).
16. W. Kutzelnigg and W. Klopper, *J. Chem. Phys.,* **94,** 1985 (1991). Wavefunctions with Terms Linear in the Interelectronic Coordinates to Take Care of the Correlation Cusp. I. General Theory.

17. D. H. Magers, R. J. Harrison, and R. J. Bartlett, *J. Chem. Phys.*, **84**, 3284 (1986). Isomers and Excitation Energies of C_4. (Approximate determination of open-shell singlet energies with triplet information.)

18. B. O. Roos, in: *Methods in Computational Physics*, Vol. 1, G. H. F. Diercksen and S. Wilson, Eds., Reidel, Dordrecht, 1983, p. 161. The Multiconfigurational (MC) SCF Method.

19. R. Shepard, *Adv. Chem. Phys.*, **69**, 63 (1987). The Multiconfiguration Self-Consistent-Field Method.

20. T. H. Dunning, Jr., D. C. Cartwright, W. J. Hunt, P. J. Hay, and F. W. Bobrowicz, *J. Chem. Phys.*, **64**, 4755 (1976). Generalized Valence Bond Calculations on the Ground State ($X^1\Sigma_g^+$) of Nitrogen.

21. G. D. Purvis, III, and R. J. Bartlett, *J. Chem. Phys.*, **76**, 1910 (1982). A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. (CCSD.)

22. J. Noga and R. J. Bartlett, *J. Chem. Phys.*, **86**, 7041 (1987). The Full CCSDT Model for Molecular Electronic Structure. Ibid., **89**, 3401 (1988). Erratum.

23. K. Ruedenberg, M. W. Schmidt, M. M. Gilbert, and S. T. Elbert, *Chem. Phys.*, **71**, 41 (1982). Are Atoms Intrinsic to Molecular Wavefunctions? I. The FORS Model.

24. G. Hose and U. Kaldor, *J. Phys., B: Atom. Mol. Phys.*, **12**, 3827 (1979). Diagrammatic Many-Body Perturbation Theory for General Model Spaces.

25. M. G. Shepard and K. F. Freed, *J. Chem. Phys.*, **75**, 4525 (1981). Convergence Studies of the Effective Valence Shell Hamiltonian for Correlation Energies of the Fluorine Atom and Its Ions Using Third Order Quasidegenerate Many-Body Perturbation Theory.

26. S. Kucharski and R. J. Bartlett, *Int. J. Quantum Chem. Symp.*, **22**, 383 (1988). Multi-Reference Many-Body Perturbation Theory.

27. D. Mukherjee and S. Pal, *Adv. Quantum Chem.*, **20**, 292 (1989). Use of Cluster Expansion Methods in the Open-Shell Correlation Problem.

28. U. Kaldor, *Theor. Chim. Acta*, **80**, 427 (1991). The Fock Space Coupled Cluster Method: Theory and Application.

29. S. Pal, M. Rittby, R. J. Bartlett, D. Dinha, and D. Mukherjee, *J. Chem. Phys.*, **88**, 4357 (1988). Molecular Applications of Multireference Coupled-Cluster Methods Using an Incomplete Model Space. Direct Calculation of Excitation Energies. (FS-MRCCSD.)

30. J. F. Stanton, R. J. Bartlett, and C. M. L. Rittby, *J. Chem. Phys.*, **97**, 5560 (1992). Fock Space Multireference Coupled-Cluster Theory for General Single Determinant Reference Functions.

31. A. Balkova and R. J. Bartlett, *Chem. Phys. Lett.*, **193**, 364 (1992). Coupled-Cluster Method for Open-Shell Singlet States.

32. J. Paldus, in *Methods in Computational Molecular Physics*, Vol. 1, S. Wilson and G. H. F. Diercksen, Eds., Plenum, New York, 1992, p. 99. Coupled Cluster Theory.

33. R. J. Bartlett and G. D. Purvis, III, *Int. J. Quantum Chem.*, **14**, 561 (1978). Many-Body Perturbation Theory, Coupled Pair Many-Electron Theory, and the Importance of Quadruple Excitations for the Correlation Problem. [SDQ-MBPT(4), CCD].

34. S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.*, **8**, 61 (1974). Configuration Interaction Calculations on the Nitrogen Molecule.

35. C. W. Bauschlicher, Jr., and P. R. Taylor, *J. Chem. Phys.*, **85**, 2779 (1986). Benchmark Full Configuration Interaction Calculations on H_2O, F, and F^-.

36. R. J. Harrison, *J. Chem. Phys.*, **94**, 5020 (1991). Approximating Full Configuration Interaction with Selected Configuration Interaction and Perturbation Theory.

37. W. von Niessen, J. Schirmer, and L. S. Cederbaum, *Comput. Phys. Rep.*, **1**, 59 (1984). Computational Methods for the One-Particle Green's Function.

38. J. Oddershede, P. Jørgensen, and D. L. Yeager, *Comput. Phys. Rep.*, **2**, 25 (1984). Polarization Propagator Methods in Atomic and Molecular Calculations.

39. C. W. Bauschlicher, Jr., S. R. Langhoff, P. R. Taylor, N. C. Handy, and P. J. Knowles, *J. Chem. Phys.*, **85**, 1469 (1986). Benchmark Full Configuration-Interaction Calculations on HF and NH_2.

40. R. J. Harrison and N. C. Handy, *Chem. Phys. Lett.*, **95**, 386 (1983). Full CI Calculations on BH, H_2O, NH_3, and HF.

41. R. J. Bartlett and D. M. Silver, *Int. J. Quantum Chem. Symp.*, **9**, 183 (1975). Some Aspects of Diagrammatic Perturbation Theory.

42. R. J. Bartlett and D. M. Silver, *Phys. Rev.*, **A10**, 1927 (1974). Pair-Correlation Energies in Sodium Hydride with Many-Body Perturbation Theory; *Chem. Phys. Lett.*, **29**, 199 (1974). Many-Body Perturbation Theory Applied to Hydrogen Fluoride.

43. R. J. Bartlett and I. Shavitt, *Chem. Phys. Lett.*, **50**, 190 (1977). Comparison of High-Order Many-Body Perturbation Theory and Configuration Interaction for H_2O.

44. S. A. Kucharski, J. Noga, and R. J. Bartlett, *J. Chem. Phys.*, **90**, 7282 (1989). Fifth-Order Many-Body Perturbation Theory for Molecular Correlation Energies.

45. J. Paldus and J. Čížek, *Adv. Quantum Chem.*, **9**, 105 (1975). Time-Independent Diagrammatic Approach to Perturbation Theory of Fermion Systems.

46. J. Cizek, *Adv. Chem. Phys.*, **14**, 35 (1969). On the Use of the Cluster Expansion and the Technique of Diagrams in Calculations of the Correlations Effects in Atoms and Molecules.

47. M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, *J. Chem. Phys.*, **83**, 4041 (1985). Towards a Full CCSDT Model for Electron Correlation. [CCSD + T(CCSD).]

48. K. Raghavachari, G. W. Trucks, M. Head-Gordon, and J. A. Pople, *Chem. Phys. Lett.*, **157**, 479 (1989). A Fifth-Order Perturbation Comparison of Electron Correlation Theories.

49. R. J. Bartlett, J. D. Watts, S. A. Kucharski, and J. Noga, *Chem. Phys. Lett.*, **165**, 513 (1990). Non-Iterative Fifth-Order Triple and Quadruple Excitation Energy Correlations in Correlated Methods. [CCSD(T), CCSD + TQ*(CCSD).] Ibid., **167**, 609 (1990). Erratum.

50. A. C. Hurley, *Electron Correlations in Small Molecules*, Academic Press, San Francisco, 1976.

51. S. A. Kucharski and R. J. Bartlett, *J. Chem. Phys.*, **97**, 4282 (1992). The Coupled-Cluster Single, Double, Triple, and Quadruple Excitation Method.

52. Y. S. Lee, S. A. Kucharski, and R. J. Bartlett, *J. Chem. Phys.*, **81**, 5906 (1984). A Coupled-Cluster Approach with Triple Excitations. (CCSDT-1.)

53. S. A. Kucharski and R. J. Bartlett, *Chem. Phys. Lett.*, **206**, 574 (1993). Coupled Cluster Methods Correct Through Sixth Order.

54. R. A. Chiles and C. E. Dykstra, *J. Chem. Phys.*, **74**, 4544 (1981). An Electron Pair Operator Approach to Coupled-Cluster Wavefunctions. Applications to He_2, Be_2, and Mg_2 and Comparison with CEPA Methods.

55. N. C. Handy, J. A. Pople, M. Head-Gordon, K. Raghavachari and G. W. Trucks, *Chem. Phys. Lett.*, **164**, 185 (1989). Size-Consistent Brueckner Theory Limited to Double Substitutions.

56. J. F. Stanton, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.*, **97**, 5554 (1992). On the Choice of Orbitals for Symmetry Breaking Problems with Application to NO_3. [Brueckner-CCD(T), QRHF-CCSD(T).]

57. D. Feller and E. R. Davidson, in *Reviews in Computational Chemistry*, Vol. 1, K. B. Lipkowitz and D. B. Boyd, Eds. VCH Publishers, New York, 1990, p. 1. Basis Sets for Ab Initio Molecular Orbital Calculations and Intermolecular Interactions.

58. P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973). The Influence of Polarization Functions on Molecular Orbital Hydrogeneration Energies. (6-31G*.)

59. J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980). Self-Consistent Molecular Orbital Methods. 21. Small Split-Valence Basis Sets for First Row Elements. (6-31G**.)

60. T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970). Gaussian Basis Functions for Use in Molecular Calculations. I. Contraction of (9s,5p) Atomic Basis Sets for the First-Row Atoms. (DZ, TZ.)

61. S. Huzinaga, *Comput. Phys. Rep.*, **2**, 279 (1985). Basis Sets for Molecular Calculations.

62. L. T. Redmon, G. D. Purvis, III, and R. J. Bartlett, *J. Am. Chem. Soc.*, **101,** 2856 (1979). Accurate Binding Energies of Diborane, Borane Carbonyl, and Borazane Determined by Many-Body Perturbation Theory. (Correlated polarization exponents for DZP basis sets.)

63. T. H. Dunning, Jr., *J. Chem. Phys.*, **55,** 716 (1971). Gaussian Basis Functions for Use in Molecular Calculations. III. Contraction of (10s,6p) Atomic Basis Sets for First-Row Atoms. (TZ.)

64. P. O. Widmark, P. A. Malmqvist, and B. O. Roos, *Theor. Chim. Acta,* **77,** 291 (1990). Density Matrix Averaged Atomic Natural Orbital (ANO) Basis Sets for Correlated Molecular Wavefunctions. I. First-Row Atoms.

65. J. Almlöf and P. R. Taylor, *Adv. Quantum Chem.*, **22,** 301 (1991). Atomic Natural Orbital (ANO) Basis Sets for Quantum Chemical Calculations.

66. T. H. Dunning, Jr., *J. Chem. Phys.*, **90,** 1007 (1989). Gaussian Basis Functions for Use in Related Molecular Calculations I. The Atoms Boron Through Neon and Hydrogen. (ccPVDZ, ccPVTZ, ccPVQZ.)

67. A. Sadlej, *Theor. Chim. Acta,* **79,** 123 (1991). Medium-Size Polarized Basis Sets for High-Level Correlated Calculations of Molecular Electric Properties. I. First-Row Atoms: H Through F. (POL1 basis.)

68. J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, *J. Chem. Phys.*, **94,** 4334 (1991). A Direct Product Decomposition Approach for Symmetry Exploitation in Many-Body Methods. I. Energy Calculations.

69. L. R. Khan, P. Baybutt, and D. G. Truhlar, *J. Chem Phys.*, **65,** 3826 (1976). Ab Initio Effective Core Potentials. Reduction of All-Electron Molecular Structure Calculations to Calculations Involving Only Valence Electrons.

70. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, **82,** 270 (1985). Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for Transition Metal Atoms Sc to Hg.

71. M. M. Hurley, L. Pacios, P. A. Christiansen, R. B. Ross, and W. C. Ermler, *J. Chem Phys.*, **84,** 6840 (1986). Ab Initio Relativistic Effective Potentials with Spin-Orbit Operators II; K Through Kr.

72. P. Pulay, *Adv. Chem. Phys.*, **69,** 241 (1987). Analytical Derivative Methods in Quantum Chemistry.

73. G. Fogarasi and P. Pulay, *Annu. Rev. Phys. Chem.*, **35,** 191 (1984). Ab initio Vibrational Force Fields.

74. R. J. Bartlett, J. F. Stanton, and J. D. Watts, in *Advances in Molecular Vibrations and Collision Dynamics,* Vol. 1, J. Bowman, Ed., JAI Press, Greenwich, CT, 1991, p. 139. Analytic MBPT(2) Energy Derivatives: A Powerful Tool for the Interpretation and Prediction of Vibrational Spectra for Unusual Molecules.

75. C. E. Dykstra, J. D. Augspurger, B. Kirtman, and D. J. Malik, in *Reviews in Computational Chemistry,* Vol. 1, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1990, p. 83. Properties of Molecules by Direct Calculation.

76. J. Gauss and D. Cremer, *Adv. Quantum Chem.*, **23,** 206 (1992). Analytical Energy Gradients in Møller–Plesset Perturbation Theory and Quadratic Configuration Interaction Methods: Theory and Application.

77. J. Gauss, J. F. Stanton, and R. J. Bartlett, *J. Chem. Phys.*, **95,** 2623 (1991). Coupled-Cluster Open-Shell Analytic Gradients: Implementation of the Direct Product Decomposition Approach in Energy Gradient Calculations.

78. J. Gauss, J. F. Stanton, and R. J. Bartlett, *J. Chem. Phys.*, **95,** 2639 (1991). Analytic Evaluation of Energy Gradients at the Coupled-Cluster Singles and Doubles Level Using Quasi-Restricted Hartree–Fock Open-Shell Reference Functions.

79. J. Gauss, W. J. Lauderdale, J. F. Stanton, J. D. Watts, and R. J. Bartlett, *Chem. Phys. Lett.*, **182,** 207 (1991). Analytic Energy Gradients for Open-Shell Coupled-Cluster Singles and Doubles (CCSD) Calculations Using Restricted Open-Shell Hartree–Fock (ROHF) Reference Functions.

80. W. J. Lauderdale, J. F. Stanton, J. Gauss, J. D. Watts, and R. J. Bartlett, *J. Chem. Phys.*, **97**, 6606 (1992). Restricted Open-Shell Hartree–Fock Based Many-Body Perturbation Theory. Theory and Application of Energy and Gradient Calculations.

81. J. D. Watts, G. W. Trucks, and R. J. Bartlett, *Chem. Phys. Lett.*, **164**, 502 (1989). Coupled-Cluster, Unitary Coupled-Cluster and MBPT(4) Open-Shell Analytical Gradient Methods.

82. J. D. Watts, J. Gauss, and R. J. Bartlett, *Chem. Phys. Lett.*, **200**, 1 (1992). Open-Shell Analytical Energy Gradients for Triple Excitation Many-Body Coupled-Cluster Methods. MBPT(4), CCSD + T(CCSD), CCSD(T) and QCISDT(T). (UHF-CC/MBPT gradients.)

83. J. D. Watts, J. Gauss, and R. J. Bartlett, *J. Chem. Phys.*, **98**, 8718 (1993). Coupled-Cluster Methods with Non-Iterative Triple Excitations for Restricted Open-Shell Hartree–Fock and Other General Single Determinant Reference Functions. Energies and Analytical Gradients. (ROHF-CCSD(T) gradients.)

84. E. A. Salter, G. W. Trucks, and R. J. Bartlett, *J. Chem. Phys.*, **90**, 1752 (1989). Analytic Energy Derivatives in Many-Body Methods. I. First Derivatives.

85. J. F. Stanton, J. D. Watts, and R. J. Bartlett, *J. Chem. Phys.*, **94**, 404 (1991). Harmonic Vibrational Frequencies and Infrared Intensities from Analytic Fourth-Order Many-Body Perturbation Theory Gradients.

86. B. H. Besler, G. E. Scuseria, A. C. Scheiner, and H. F. Schaefer, III, *J. Chem. Phys.*, **89**, 360 (1988). A Systematic Theoretical Study of Harmonic Vibrational Frequencies: The Single and Double Excitation Coupled Cluster Model.

87. J. R. Thomas, J. B. DeLeeuw, G. Vacek, and H. F. Schaefer, III, *J. Chem. Phys.*, **98**, 1336 (1993). A Systematic Study of the Harmonic Vibrational Frequencies for Polyatomic Molecules. The Single, Double, and Perturbative Triple Excitation Coupled-Cluster [CCSD(T)] Method.

88. J. D. Head and M. C. Zerner, *Adv. Quantum Chem.*, **20**, 241 (1988). Newton-Based Optimization Methods for Obtaining Molecular Conformation.

89. T. Schlick, in *Reviews in Computational Chemistry,* Vol. 3, K. B. Lipkowitz and D. B. Boyd, Eds., VCH Publishers, New York, 1992, pp. 1–71. Optimization Methods in Computational Chemistry.

90. R. Hoffmann and R. B. Woodward, *Acc. Chem. Res.* **1**, 17 (1968). The Conservation of Orbital Symmetry.

91. N. C. Handy, R. D. Amos, J. F. Gaw, J. E. Rice, E. D. Simandiras, T. J. Lee, R. J. Harrison, W. D. Laidig, G. B. Fitzgerald, and R. J. Bartlett, *Geometrical Derivatives of Energy Surfaces and Molecular Properties,* P. Jørgensen and J. Simons, Eds., Reidel, Dordrecht, 1986, p. 179. Techniques Used in Evaluating Orbital and Wavefunction Coefficients and Property Derivatives [e.g., the evaluation of M(B)P(T)-2 second derivatives].

92. J. F. Stanton, J. Gauss, and R. J. Bartlett, *Chem. Phys. Lett.*, **195**, 194 (1992). Analytic Evaluation of Second Derivatives Using Second-Order Many-Body Perturbation Theory and Unrestricted Hartree–Fock Reference Functions.

93. J. Gauss, J. F. Stanton, and R. J. Bartlett, *J. Chem. Phys.*, **97**, 7825 (1992). Analytic (ROHF)-MBPT(2) Second Derivatives.

94. D. H. Magers, E. A. Salter, R. J. Bartlett, C. Salter, B. A. Hess, and L. J. Schaad, *J. Am. Chem. Soc.*, **110**, 3435 (1988). Do Stable Isomers of N_3H_3 Exist?

95. K. F. Ferris and R. J. Bartlett, *J. Am. Chem. Soc.*, **114**, 8302 (1992). Hydrogen Pentazole: Does It Exist?

96. T. R. Burkholder, L. Andrews, and R. J. Bartlett, *J. Phys. Chem.*, **97**, 3500 (1993). Reaction of Boron Atoms with Carbon Dioxide. Matrix and Ab Initio Calculated Infrared Spectra of OBCO.

97. W. H. Green, A. Willetts, D. Jayatilaka, and N. C. Handy, *Chem. Phys. Lett.*, **169**, 127 (1990). Ab Initio Prediction of Fundamental, Overtone and Combination Band Infrared Intensities.

98. Y. Yamaguchi, M. Frisch, J. Gaw, H. F. Schaefer, III, and J. S. Binkley, *J. Chem. Phys.*, **84**, 2262 (1986). Analytic Evaluation and Basis Set Dependence of Intensities of Infrared Spectra.
99. S. R. Gwaltney and R. J. Bartlett, *J. Chem. Phys.*, in press. Comment on: The Relation Between Intensity and Dipole Moment for Bending Modes in Linear Molecules.
100. E. D. Simandiras, J. E. Rice, T. J. Lee, R. D. Amos, and N. C. Handy, *J. Chem. Phys.*, **88**, 3187 (1988). On the Necessity of f-Basis Functions for Bending Frequencies.
101. M. E. Jacox, *J. Phys. Chem.*, **91**, 6595 (1987). Vibrational and Electronic Spectra of the H+HCN Reaction Products Trapped in Argon.
102. J. F. Stanton, W. N. Lipscomb, D. H. Magers, and R. J. Bartlett, *J. Chem. Phys.*, **90**, 1077 (1989). Highly Correlated Single-Reference Studies of the O_3 Potential Surface. I. Effects of High Order Excitations on the Equilibrium Structure and Harmonic Force Field of Ozone.
103. T. J. Lee, W. D. Allen, and H. F. Schaefer, III, *J. Chem. Phys.*, **87**, 7063 (1987). The Analytic Evaluation of Energy First Derivatives for Two-Configuration Self-Consistent Field Configuration Interaction Wavefunctions. Applications to Ozone and Ethylene.
104. S. M. Alder-Golden, S. R. Langhoff, C. W. Bauschlicher, and G. D. Carney, *J. Chem. Phys.*, **83**, 255 (1985). Theoretical Calculation of Ozone Vibrational Frequencies (CASSCF).
105. K. Raghavachari, G. W. Trucks, J. A. Pople, and E. Replogle, *Chem. Phys. Lett.*, **158**, 207 (1989). Highly Correlated Systems: Structure, Binding Energy and Harmonic Vibrational Frequencies of Ozone.
106. J. D. Watts, J. F. Stanton, and R. J. Bartlett, *Chem. Phys. Lett.*, **178**, 471 (1991). A Benchmark Coupled-Cluster Single, Double, and Triple Excitation (CCSDT) Study of the Structure and Harmonic Vibrational Frequencies of the Ozone Molecule.
107. D. H. Magers, W. N. Lipscomb, R. J. Bartlett, and J. F. Stanton, *J. Chem. Phys.*, **91**, 1945 (1989). The Equilibrium Structure and Harmonic Vibrational Frequencies of Ozone: Coupled-Cluster Results Including Triple Excitations.
108. T. J. Lee and G. E. Scuseria, *J. Chem. Phys.*, **93**, 489 (1990). Vibrational Frequencies of Ozone.
109. R. J. Bartlett, I. Shavitt, and G. D. Purvis, III, *J. Chem. Phys.*, **71**, 281 (1979). The Quartic Force Field of H_2O Determined by Many-Body Methods That Include Quadruple Excitation Effects.
110. R. J. Bartlett, S. J. Cole, G. D. Purvis, III, W. C. Ermler, H. C. Hsieh, and I. Shavitt, *J. Chem. Phys.*, **87**, 6579 (1987). The Quartic Force Field of H_2O Determined by Many-Body Methods. II. Effects of Triple Excitations.
111. J. M. Bowman, A. Wierzbicki, and J. Zuniga, *Chem. Phys. Lett.*, **150**, 269 (1988). Exact Vibrational Energies of Non-Rotating H_2O and D_2O Using an Accurate Ab Initio Potential.
112. M. Rittby and R. J. Bartlett, *J. Phys. Chem.*, **92**, 3033 (1988). An Open-Shell Spin-Restricted Coupled Cluster Method: Application to Ionization Potentials in N_2. (ROHF-CCSD, ROHF-CCSDT-1, QRHF-CCSD.)
113. R. L. Martin and D. A. Shirley, in *Electron Spectroscopy: Theory, Techniques and Applications*, C. R. Brundle and A. D. Baker, Eds., Academic Press, New York, 1977, p. 75. Many-Electron Theory of Photoemission.
114. J. Geertsen, C. M. L. Rittby, and R. J. Bartlett, *Chem. Phys. Lett.*, **164**, 57 (1989). The Equation-of-Motion Coupled-Cluster Method: Excitation Energies of Be and CO.
115. D. C. Comeau and R. J. Bartlett, *Chem. Phys. Lett.*, **207**, 414 (1993). The Equation-of-Motion Coupled-Cluster Method: Application to Open- and Closed-Shell Reference States.
116. J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.*, **98**, 7029 (1993). The Equation-of-Motion Coupled-Cluster Method. A Systematic Biorthogonal Approach to Molecular Excitation Energies, Transition Probabilities and Excited State Properties.
117. J. D. Watts, M. Rittby, and R. J. Bartlett, *J. Am. Chem. Soc.*, **111**, 4155 (1989). Calculation of Molecular Ionization Potentials Using Single- and Multi-reference Coupled-Cluster Methods. Application to Methylenimine, CH_2NH and Methylenephosphine, CH_2PH.

118. S. Pal, M. Rittby, and R. J. Bartlett, *Chem. Phys. Lett.*, **160**, 212 (1989). Multi-Reference Coupled-Cluster Methods of Ionization Potentials with Partial Inclusion of Triple Excitations.

119. J. D. Watts, J. Gauss, J. F. Stanton, and R. J. Bartlett, *J. Chem. Phys.*, **97**, 8372 (1992). Linear and Cyclic Isomers of C_4. A Theoretical Study with Coupled-Cluster Methods and Large Basis Sets.

120. J. D. Bolcer and R. B. Hermann, this volume.

121. C. W. McCurdy, Jr., T. N. Rescigno, D. L. Yeager, and V. McKoy, in *Modern Theoretical Chemistry III*, H. F. Schaefer, III, Ed., Plenum, New York, 1977. The Equation of Motion Method: An Approach to the Dynamical Properties of Atoms and Molecules.

122. J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.*, **98**, 9335 (1993). Does Chlorine Peroxide Exhibit a Strong Ultraviolet Absorption Near 250 nm? (EOM-CCSD for excitation energies.)

123. C. M. L. Rittby and R. J. Bartlett, *Theor. Chim. Acta*, **80**, 469 (1991). Multireference Coupled-Cluster Theory in Fock Space With an Application to s-Tetrazine.

124. H. Nakatsuji, *Acta Chimica Hungarica. Models in Chemistry*, **129**, 719 (1992). Electronic Structures of Ground, Excited, Ionized and Anion States Studied by the SAC/SAC-CI Theory.

125. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1988). A Basis Set for Correlated Wavefunctions. (6-311G**).

126. R. McWeeny, in *Molecules in Physics, Chemistry, and Biology*, J. Maruani, Ed., Reidel, Dordrecht, 1989, p. 1. The Molecule as a Many-Electron System: Electron Densities and Molecular Properties.

127. D. Feller, C. M. Boyle, and E. R. Davidson, *J. Chem. Phys.*, **86**, 3424 (1987). One-Electron Properties of Several Small Molecules Using Near-Hartree–Fock Limit Basis Sets.

128. H. Sekino and R. J. Bartlett, *J. Chem. Phys.*, **82**, 4225 (1985). Spin Density of Radicals by Finite Field Many-Body Methods.

129. S. A. Perera, J. D. Watts, and R. J. Bartlett, to be published. Analytical Coupled-Cluster Evaluation of Spin Densities.

130. H. Sekino and R. J. Bartlett, *J. Chem. Phys.*, **98**, 3022 (1993). Molecular Hyperpolarizabilities.

131. S. A. Perera and R. J. Bartlett, *Chem. Phys. Lett.*, in press. Relativistic Effects at the Correlated Level: An Application to Interhalogens.

132. S. A. Perera and R. J. Bartlett, *Phys. Rev.*, submitted. Nuclear Quadrupole Moments from Accurate Coupled-Cluster Electric Field Gradients.

133. J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.*, in press. A Coupled-Cluster Based Effective Hamiltonian Method for Dynamic Electric Polarizabilities.

134. R. D. Amos, *Adv. Chem. Phys.*, **67**, 99 (1987). Molecular Property Derivatives.

135. R. Ditchfield, *Mol. Phys.*, **27**, 789 (1974). Self-Consistent Perturbation Theory of Diamagnetism. I. A Gauge-Invariant LCAO Method for NMR Chemical Shifts.

136. M. Schindler and W. Kutzelnigg, *J. Chem. Phys.*, **76**, 1919 (1982). Theory of Magnetic Susceptibilities and NMR Chemical Shifts in Terms of Localized Quantities. II. Application to Some Simple Molecules.

137. T. D. Bouman and A. E. Hansen, *Int. J. Quantum Chem. Symp.*, **23**, 381 (1989). Linear Response Calculations of Molecular Optical and Magnetic Properties Using Program RPAC: NMR Shielding Tensors of Pyridine and *n*-Azines.

138. K. Wolinski, J. F. Hinton, and P. Pulay, *J. Am. Chem. Soc.*, **112**, 8251 (1990). Efficient Implementation of the Gauge-Independent Atomic Orbital Method for NMR Chemical Shift Calculations.

139. J. Gauss, *Chem. Phys. Lett.*, **191,** 614 (1992). Calculation of NMR Chemical Shifts as Second-Order Many-Body Perturbation Theory Using Gauge Including Atomic Orbitals.

140. J. Paldus, J. Čížek, and B. Jeziorski, *J. Chem. Phys.*, 90, 4356 (1989). Coupled-Cluster Approach or Quadratic Configuration Interaction?