

APPLICATION OF THE CI-SINGLES METHOD IN PREDICTING THE ENERGY, PROPERTIES, AND REACTIVITY OF MOLECULES IN THEIR EXCITED STATES

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ABSTRACT Configuration interaction with all single excited determinants, CIS, is an easy to use, cost effective method for surveying many excited states of chemical interest. Geometry optimization and vibrational frequency calculations can be carried out using analytical gradients, energy differences can be improved by second order perturbation theory, and large systems can be studied by direct methods. The capabilities and limitations of CIS are illustrated by calculations on the excitation energies of benzene, bicyclobutane and Li_2Na_2 , optimized geometry and properties of $n-\pi^*$ excited state of formaldehyde, vibrational frequencies of $n-\pi^*$ excited acrolein, and excited state potential energy curves for breaking σ and π bonds. These examples are also used to discuss the practical aspects of CIS calculations.

1. Introduction

The intent of this Chapter is to discuss some applications and practical aspects of the calculation of excited states by configuration interaction involving all single excitations, CIS. While this approach may not be suitable for all the excited states of a given molecule, one may hope that CIS is qualitatively correct for many excited states of chemical interest.

Just as Hartree-Fock theory is a good zeroth-order theory for the electronic structure of many ground state systems, CIS should be an adequate zeroth-order approximation for a variety of molecular excited states and should be capable of making semi-quantitative predictions. Like Hartree-Fock theory, CIS is well defined, is suitable for surveying a wide variety of systems, and can be applied to large molecules. Highly accurate descriptions of excited states require treatments beyond CIS, just as accurate

ground state calculations must go beyond the one determinantal, Hartree-Fock method. Most high quality studies of excited states involve multi-configurational SCF calculations (MCSCF) followed by extensive multi-reference CI treatments (MR-CI). Such calculations are beyond the scope of this Chapter and the reader is directed to a number of recent books and chapters for discussions of photochemistry, potential energy surfaces of excited states and MCSCF and MR-CI calculations.¹ The CIS approach is not intended to compete with these large scale calculations on small molecules used by specialists in electronic structure theory. Instead, CIS calculations provide a 'black box' method suitable for use by many chemists who are interested in obtaining semi-quantitative information about the excited states of the systems they study.

This Chapter is divided into four major sections. The first briefly outlines the theory for CIS energies gradients and properties. The next gives some examples of excitation energies and some of the practical aspects of carrying out CIS calculations. The third section examines geometries and properties of some excited states, and the final section briefly looks at some very simple photochemical processes.

2. Theory

The CIS method for the calculation of excitation energies has been discussed previously under several names, including single excitation configuration interaction (SECI) and the Tamm-Dancoff approximation (TDA). The approach used in the present Chapter has been discussed in reference 2, which should be consulted for details and leading references. Reference 2 is also the first paper to implement CIS gradients efficiently, as well as perturbative correlation corrections to CIS. In what follows, we briefly describe the background theory necessary to understand CIS calculations, using the conventional subscript notation. Atomic basis functions are labeled by the Greek letters while molecular basis quantities are labeled with either i,j,k,l or a,b,c,d for occupied and unoccupied orbitals, respectively. Here, occupied and unoccupied status refers to the ground reference state only.

CIS is based upon a simple Hartree-Fock wavefunction as the reference for the ground state of the system. If n is the number of electrons, this is a determinant of n molecular orbitals (MO):

$$\Psi_{\text{HF}} = (n!)^{-1/2} \det \{ \chi_1 \chi_2 \dots \chi_i \chi_j \dots \chi_n \}$$

These molecular orbitals are each linear combinations of N atomic orbital (AO) basis functions. Consider now one of the $n \times (N-n)$ possible singly excited determinants made by replacing an occupied orbital with an unoccupied orbital:

$$\Psi_{\text{ia}} = (n!)^{-1/2} \det \{ \chi_1 \chi_2 \dots \chi_a \chi_j \dots \chi_n \}$$

The CIS excited state wavefunction is written as a linear combination of all of the singly excited determinants possible:

$$\Psi_{\text{CIS}} = \sum_{ia} a_{ia} \Psi_{ia}$$

These configuration interaction (CI) coefficients can be deduced as normalized eigenvectors of the Hamiltonian matrix,

$$\langle \Psi_{ia} | H | \Psi_{jb} \rangle = [E_{\text{HF}} + \epsilon_a - \epsilon_i] \delta_{ij} \delta_{ab} - (\text{jallib})$$

Here ϵ represents the one-electron energy of an orbital and (jallib) are the usual two-electron integrals, transformed to the MO basis. The eigenvalues of this matrix are the CIS total energies for various excited states. Because of the simple nature of the matrix elements, diagonalization can be carried out in a direct fashion, i.e. without the storage of the 2 electron integrals. This opens the possibility of studying the excited states of molecules much larger than can be treated by methods such as MR-CI, since they involve the evaluation of more complicated matrix elements than above.

Of critical importance in complete studies of excited states is the ability to evaluate the gradient of the CIS energy. This allows the evaluation of properties such as the dipole moment or optimized geometric parameters of the excited state. Our gradient implementation involves several computational procedures and enhancements that have been suggested by others³ in the general context of CI and derivative theories. Gaussian 92⁴ also has the ability to perform CIS gradient calculations within the frozen core approximation⁵ or within the space of any user-specified window of orbitals. This is an improvement over the initial gradient implementation² which was restricted to the full CIS space.

The first derivative of the CIS energy with respect to any external system parameter (for example, a geometric variable or an applied electric field) can be written as a sum of four terms:

$$E^x = \sum_{\mu\nu\lambda\sigma} \Gamma_{\mu\nu\lambda\sigma}^{\text{CIS}} (\mu\nu | \lambda\sigma)^x + \sum_{\mu\nu} P_{\mu\nu}^{\text{CIS}} H_{\mu\nu}^x + \sum_{\mu\nu} W_{\mu\nu}^{\text{CIS}} S_{\mu\nu}^x + V_{\text{nuc}}^x$$

The first term is the contraction of the two-particle density matrix, Γ , with the AO derivative integrals. The second term is the contraction of the CIS generalized density matrix, P , with the core Hamiltonian derivatives. The third term is the overlap (S) derivative contribution. Finally, the last term is the derivative of the nuclear repulsion energy. Like the energy, the gradient can be calculated by conventional or direct means.

Because of its importance in calculating accurate one-electron properties, the generalized CIS density matrix deserves a bit more attention. It is a sum of Hartree-Fock and excited state terms:

$$P_{\mu\nu}^{\text{CIS}} = P_{\mu\nu}^{\text{HF}} + P_{\mu\nu}^{\Delta}$$

Here we have introduced P^{Δ} , the CIS delta density matrix. This can also be called a "difference density matrix," since it represents the changes in electronic distribution upon excitation. It is best described in the MO basis. There are contributions from the occupied-occupied sub-block,

$$P_{ij}^{\Delta} = - \sum_{ab} a_{ia} a_{jb}$$

the unoccupied-unoccupied sub-block,

$$P_{ab}^{\Delta} = + \sum_{ij} a_{ia} a_{jb}$$

and an unoccupied-occupied sub-block, found by solving the following set of linear equations,

$$L_{ai} = \sum_{bj} [(ij \parallel ab) - (ib \parallel ja)] P_{bj}^{\Delta} + (\epsilon_a - \epsilon_i) P_{ai}^{\Delta}$$

where the L vector is the CIS Lagrangian given in reference 2. The appearance of these off-diagonal block elements in the generalized density matrix can be interpreted as orbital relaxation following the initial gross charge rearrangement due to excitation. That is to say, the CI coefficients will by themselves describe some of the gross features of charge redistribution in the excited state, but the response of the Hartree-Fock molecular orbital coefficients to an external perturbation will account for further refinement in electronic properties. Without these off-diagonal terms, the density is simply the usual one-particle CI density matrix (1PDM).

The CIS generalized density matrix emerges naturally from writing the gradient expression as above. Contraction of this matrix with any one-electron operator yields the value for that property as an analytic derivative. For instance, the dipole moment of the excited state is calculated by the dot product of this matrix with the dipole integrals. In addition, contour plots of this density or the difference between it and the ground state density matrix are useful for visualizing what electronic changes occur upon excitation. Many conventional programs utilize instead the 1PDM as an approximation to the generalized density. Later we will show that the 1PDM is an inadequate approximation when using a truncated CI expansion.

Since the CIS level of theory has been suggested as an adequate zeroth-order approximation to many excited states, it would be useful to have an additional expression which attempts to access what influence the mixing in of other determinants has on the energy and properties of the excited state. These effects might be included in a manner

similar to the ground state correlation correction given by Møller-Plesset perturbation theory:

$$\Delta E_{\text{CIS-MP2}} = -\frac{1}{4} \sum_{ijab} \frac{\langle \Psi_{\text{CIS}} | H | \Psi_{ijab} \rangle^2}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j - \Delta_{\text{CIS}}} - \frac{1}{36} \sum_{ijkabc} \frac{\langle \Psi_{\text{CIS}} | H | \Psi_{ijkabc} \rangle^2}{\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_i - \epsilon_j - \epsilon_k - \Delta_{\text{CIS}}}$$

Here Δ_{CIS} is the CIS excitation energy. It is important to note that this expression is not derivable from standard perturbation theory but is simply suggested as one way to access the influence of higher determinants on the CIS energy. The matrix elements of the numerator have been elaborated previously^{2,6} and are used in other correlated methods. This method is size-consistent, but not variational. A corrected excitation energy can be calculated by taking the difference in this energy from the ground state MP2 energy.

3. Excitation Energies

In this section we discuss the ability of the CIS technique to reproduce experimental vertical excitation energies for chemical systems. Detailed examinations of each system have already been presented. The reader should consult these papers for more in depth discussions and more complete lists of references.

Benzene is every organic chemist's model system for understanding excited states. It also serves as an excellent example to show the strengths, weaknesses, and pitfalls of CIS calculations. Because of the high symmetry of the molecule, care must be exercised in producing initial guess vectors for the configuration interaction procedure. All symmetry types must be present for a systematic search of the lowest excited states. In comparing results to experimental data, one must be aware of the existence of symmetry-forbidden valence states observed in optical spectra as well as diffuse states observed in more elaborate multi-photon ionization (MPI) experiments.

Table 1: CIS Vertical Excitation Energies [eV] of Benzene

State	6-31G*	f	6-31+G*	f	Exp.
¹ B _{2u} π-π*	6.291	0.0	6.098	0.0	4.9
¹ B _{1u} π-π*	6.476	0.0	6.248	0.0	6.2
¹ E _{1g} π-3s			7.101	0.0	6.33
¹ A _{2u} π-3p			7.420	0.1	6.93
¹ E _{2u} π-3p			7.728	0.0	6.95
¹ E _{1u} π-π*	8.524	1.1	7.891	1.0	7.0

Table 1 contains the calculated CIS frozen-core vertical excitation energies and oscillator strengths (f) for benzene obtained by using a split valence basis set with polarization functions (6-31G*) and a basis set containing diffuse functions (6-31+G*). The geometry used here is the MP2/6-31G* theoretical structure (CC=1.3952Å, CH=1.0871Å). Experimental results are taken from reference 7. Using a 6-31G* basis, only three excited singlet states are seen below 9 eV. These correspond to the well known valence states involving the doubly degenerate HOMOs and LUMOs of the molecule. The first two possess zero oscillator strengths but non-zero experimental intensities as a result of vibrational coupling.⁸ The highest state has a relatively large oscillator strength (due to a transition moment in the plane of the molecule) and corresponds to the very intense peak in the optical spectrum.

Moving to the 6-31+G* basis set introduces new low-lying unoccupied orbitals between the degenerate HOMOs and LUMOs of benzene. The presence of these diffuse orbitals reduces the energy of the three original valence states (as they take on more diffuse character) and generates three new excited states below the intense $^1E_{1u}$ valence state. These involve excitations from the π HOMOs directly into the diffuse LUMOs and are called "Rydberg-like" since they resemble excitations in atoms. One of these Rydberg states, $^1A_{2u}$, has a non-zero oscillator strength, but because the transition moment is perpendicular to the plane of the molecule, it is not observed in the optical spectrum. MPI experiments have been used to locate these additional states, and indeed they fall between the second and the third optically seen states.

Thus, one must be careful in comparing calculated CIS energies with experimental data. There may be states with zero oscillator strengths which are seen in optical spectra, just as there may be states with non-zero oscillator strengths which are not seen. Diffuse functions may be important to obtain the complete manifold of excited states for a molecule. Discrepancies in the energetic results of the Rydberg states would most likely be reduced further with the addition of more diffuse functions to the basis set. Certain states, however, have energies which are quite high in comparison to experiment regardless of the basis set used (for example the $^1B_{2u}$ state of benzene). It has been shown that this deficiency is related to the neglect of higher excitations (beyond single excitations) in the configuration interaction.⁹ Still, the correct ordering of states and relatively good energetic results are obtained using the less computationally intensive CIS model.

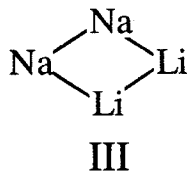
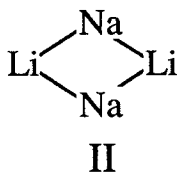
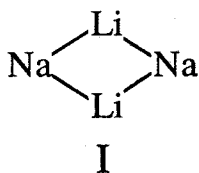
The results for benzene suggest that CIS may have some utility in studying excited organic molecules. Is this still the case for more strained hydrocarbons? Walters et al.¹⁰ used extensive CIS calculations in order to better understand the MPI spectrum of bicyclobutane. They found that for this system, the distinction between valence and Rydberg states is meaningless. The theoretical calculations along with the experimental data support the claim that all the states of bicyclobutane are diffuse (approximating atomic-like excited states) with well defined vibrational structure. Their evidence also suggests that this is a general trend for molecules of this type. In any event, the CIS technique proved invaluable in interpreting the spectra. Table 2 lists some of their results for

Table 2: Vertical Excitation Energies [eV] of Bicyclobutane

State	CIS/6-311(2+)G*	f	CIS-MP2/6-311(2+)G*	Exp.
2A ₁ (1s)	6.79	.001	6.61	6.1
3A ₁ (2p _z)	7.16	.045	6.88	6.6
1B ₁ (2p _x)	7.19	.043	7.00	6.6
1B ₂ (2p _y)	7.38	.000	7.00	-

bicyclobutane. Here the MP2/6-31G* geometry is used along with a triple-zeta with polarization basis set with two sets of diffuse functions on carbon atoms (6-311(2+)G*). Experience showed that diffuse and polarization functions on the hydrogens had little effect on energies, but that the extra diffuse function on the carbon atoms had dramatic effect. Also listed in Table 2 are the CIS-MP2 excitation energies. In this case, they systematically improve the results in correlation to experiment. The effect of higher excitations is largest for the excitation to the 2p_y orbital. However, a word of caution is due here. Our experience has shown that the CIS-MP2 theory works well for Rydberg states, but can give much worse results for valence excited states, such as the π - π^* states of pyridine.² Oscillator strengths reported in Table 2 also correspond well to the observed MPI spectrum.

To illustrate the usefulness of CIS further, let us consider an example from inorganic chemistry. Dahlseid et al.¹¹ have studied the CIS excited states of Li, Na, and mixed Li-Na clusters. One of the most interesting cases is the cluster, Li₂Na₂, which can exist in one of three planar isomeric forms:



It is known¹¹ that the most distinguishing feature of the electronic spectrum of Li₂Na₂ in comparison to other clusters of this type is that the A and B bands (the first two excited singlet states) have similar intensity. Table 3 lists the calculated CIS vertical excitation energies for each of these isomers using the RHF/6-31G* structures and a 6-31+G* basis set. These have been estimated from Figure 6 of reference 11 and state designations of only the highest symmetry isomer are used for consistency. Oscillator strengths and

Table 3: CIS Singlet Vertical Excitation Energies [eV] for Li_2Na_2

State	I	f(rel)	II	f(rel)	III	f(rel)	Exp.	f(rel)
1B _{1u}	1.72	1.0	1.84	1.0	1.78	1.0	1.75	1.0
2B _{1u}	2.15	0.7	2.18	0.3	2.16	0.4	2.02	0.8
1B _{2u}	2.35	0.3	2.36	0.3	2.34	0.2	2.38	0.1

intensities are reported in reference to the lowest excited state (taken as 1). All three isomers have virtually identical theoretical spectra, however, only isomer I yields a CIS spectrum which has intensities similar to the experimental results. The predominance of this isomer is also suggested by thermodynamic arguments.¹¹ Thus, excellent results have been obtained for the low-lying electronic states of these types of clusters using CIS theory.

4. Structures and Properties of Excited States

The vertical excitation energy is simply one of the many features of a molecular excited state which are of interest to chemists. Other information (such as the dipole moment and geometric relaxation) is harder to obtain experimentally and so theory can play a key role in understanding such details.

Table 4: CIS Properties^a of the Singlet $n-\pi^*$ State of Formaldehyde

Basis Set	C=O	C-H	H-C-H	θ	$\mu_{1\text{PDM}}$	μ_{resp}	$\Delta E_{\text{adiab.}}$
STO-3G	1.309	1.085	117.9	30.1	-1.067	0.338	3.71
6-31G	1.280	1.076	121.3	0.0	0.579	1.673	3.99
6-31+G	1.278	1.077	121.4	0.0	0.646	1.646	3.97
6-31G*	1.258	1.085	117.6	27.9	0.375	1.371	4.44
6-31+G*	1.255	1.085	118.3	24.9	0.476	1.373	4.40
Expt.	1.321	1.092	121.5	20.5		1.56	3.5

^aunits: distances in Å, angles in degrees, dipole moments in Debye, and energies in eV

Consider first the CIS results on another fundamental and well-studied system: formaldehyde. Table 4 lists the calculated CIS properties of the $n-\pi^* \ ^1A_2$ state of this system.² Geometric parameters have all been optimized on the potential surface of this electronic state using analytic gradients. All electrons have been included in the CI. The out-of-plane bending angle, θ , is non-zero at most levels of theory (in agreement with experiment), however it appears to be critical to have the polarization functions in the basis set in order to predict this. This is in accord with ground state bending angles (like that of ammonia). Adiabatic transition energies have been computed as the difference between the optimized ground and excited state energies, including calculated zero-point vibrational energies (CIS frequencies are obtained by numerical differentiation of the analytical gradients). As mentioned in the theory section, one might choose one of two theoretical definitions for the electronic density of the excited state: the one-particle density matrix (1PDM) or the density derived as a response to any external perturbation (resp). It is clear that in this case the 1PDM dipole moment severely overestimates the amount of charge transferred from the oxygen to the π system. The response density corrects this nicely. Overall agreement to experiment and previous theoretical work is quite good for this prototypical system. Semi-quantitative structural information has been obtained, even though the adiabatic transition energy is almost an electron volt too high (an error in CIS which is typical of valence excited states). Rydberg excited states, discussed in detail in reference 2, produce even better agreement with experiment for formaldehyde.

The interpretation of vibrational structure on electronic spectra is a venerable task. Here is another area where theoretical calculations may be of assistance. Consider the $n-\pi^*$ state of trans acrolein (propenal). Birge et al.¹² have assigned the principle vibrational modes of the excited state. Their data appears in Table 5 along with our calculated CIS frequencies obtained using a 6-31G* basis set. Here the optimized theoretical geometry has been used (C=O 1.2577 Å, C-C 1.4524 Å, C=C 1.3298 Å, OCC 123.48°, CCC 124.57°) and all electrons have been included. This is a planar structure with no imaginary frequencies (CIS energy=-190.59219 a.u., zero-point vibrational energy=0.06268 a.u.). Many of the assignments of Birge et al.¹² have been confirmed. Absolute frequencies are very much higher than experiment, but this is to be expected since it is known that HF frequencies for the ground state must be scaled in order to compare them to experiment. The linear fit of the CIS frequencies given in Figure 1 is $\nu = 0.74 \nu_{\text{calc}} + 77.5$ (correlation coefficient = 0.95).

In closing this section, we offer a few hints regarding the optimization of excited state geometries using CIS. First, because the excited state surface may differ drastically from the ground state surface, the use of ground state force constants in an optimization may be counterproductive. Numerically estimating force constants for several key variables may improve convergence greatly. Second, because the CIS excited state wavefunction depends on an HF ground state reference, there may be difficult cases where

Table 5: Trans Acrolein $n-\pi^*$ Excited State Frequencies [cm^{-1}]

Mode	CIS/6-31G*	Expt.
A''	168	250
A''	435	333
A' CCO bend	526	488
A''	680	582
A''	986	644
A''	1108	909
A'	1193	1133
A' C=O Str.	1670	1266
A' C=C Str.	1794	1410

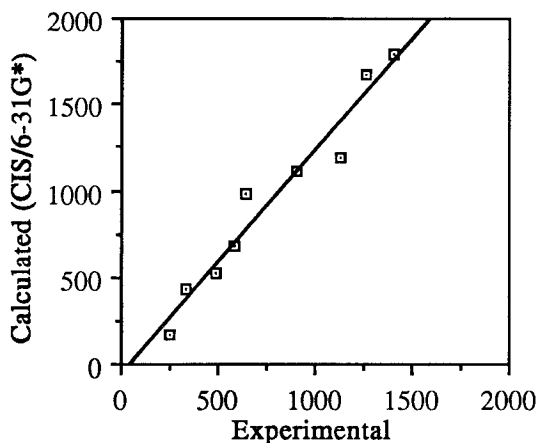


Figure 1. Comparison of calculated and experimental vibrational frequencies for the $n-\pi^*$ excited state of *trans* acrolein.

the structure is quite distorted from the ground state equilibrium geometry and a HF solution may be either difficult to find or inappropriate. For most cases, simply using a more sophisticated SCF procedure (such as quadratic convergence, QCSCF) may be sufficient to determine the reference. For instance, the $\pi-\pi^*$ perpendicular state of ethylene has D_{2d} symmetry, but this geometry does not lead to a single determinant for the ground

state (see reference 13). An approximate D_{2d} symmetry structure which is actually D_2 symmetry may be used to study this state. Finally, since the CIS procedure leads directly to a variety of excited states, following the state of interest during a geometry optimization may be confusing. For instance, the second excited vertical state may become the first excited state at the optimized geometry of that state. Our implementation takes as the guess for the CI, the density from the last geometry point and follows that state. Still, there is the possibility that significant mixing among states in distorted geometries will cause the optimization procedure to jump from state to state (either in the ground state HF or in the CIS part of the calculation). Monitoring large energy and wavefunction changes will usually allow these occasions to be obvious, and a restart of the optimization may be required using QCSCF to get the correct ground state reference or marking a new state to follow in the CI.

5. Potential Energy Surfaces of Excited States

In this section we examine CIS calculations on some prototypical potential energy curves for breaking σ and π bonds. The simplest treatment of these systems that gives qualitatively correct results is a small, state averaged multi-configuration SCF calculation. Such computations serve as a reference for the CIS approach. Both the spin-restricted and spin-unrestricted forms of CIS have been used to calculate the lowest excited singlet and triplet potential energy curves for stretching the σ bond in H_2 and LiH , and for twisting the π bond in C_2H_4 and CH_2NH .

The ground and excited state potential energy curves for stretching the bond in H_2 , shown in Figure 2, serve as a model for non-polar bond dissociation. The CIS calculations are compared to complete active space MC-SCF (CASSCF) calculations with 2 electrons in 2 orbitals, state averaged for the ground state and the first excited single, using the 6-31G** basis set. The CASSCF triplet in this space is identical to ROHF. For the spin restricted case (Fig. 2a), the RHF ground state displays the well known problem of dissociating to the wrong limit. Despite the difficulties with the RHF reference, the RCIS singlet and triplet curves agree very well with the CASSCF results. Figure 2b shows the behavior of the spin unrestricted calculations. The ground state UHF curve qualitatively dissociates to the correct limit, but the wavefunction has serious problems with spin contamination for bond lengths greater than ca. 1.1\AA . The UCIS singlet is in good agreement with the CASSCF calculation. However, the UCIS triplet is qualitatively incorrect beyond the RHF/UHF instability, and approaches the lowest excited singlet rather than the ground state as the bond is elongated. This suggests strongly that UCIS should be avoided for states with spin higher than the ground state.

Figure 3 shows the potential energy curves for LiH as a model for polar bonds. The CASSCF calculations are analogous to those for H_2 . The RCIS singlet and triplet qualitatively have the correct shape. The agreement is not as good as for H_2 probably because double excitations make a significant contribution to the CASSCF calculations. The UCIS curves (not shown) are similar to the problems found for H_2 .

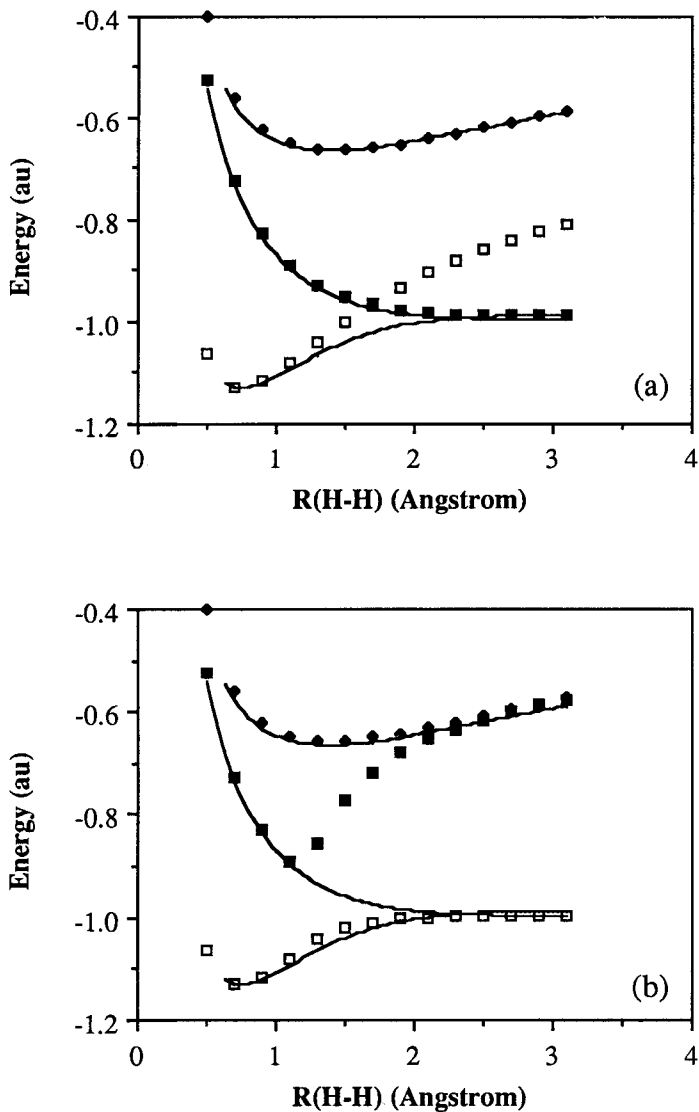


Figure 2. Comparison of CIS and CASSCF potential energy curves for H₂ dissociation (a) spin restricted, (b) spin unrestricted (open squares - RHF or UHF ground state, diamonds - RCIS or UCIS singlet, filled squares - RCIS or UCIS triplet, solid lines - 2 electron, 2 orbital state averaged CASSCF).

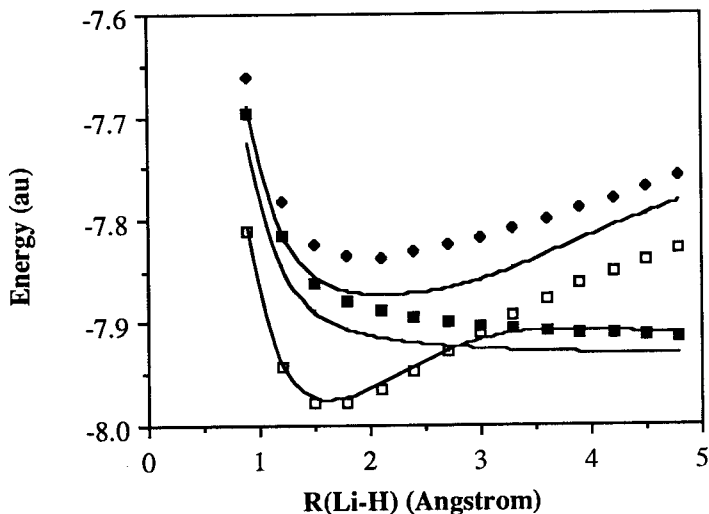


Figure 3. Comparison of spin restricted CIS and CASSCF potential energy curves for LiH dissociation (open squares - RHF ground state, diamonds - RCIS singlet, filled squares - RCIS triplet, solid lines - 2 electron, 2 orbital state averaged CASSCF).

The potential energy curves for twisting the pi bond in ethylene are presented in Figure 4. Like the above calculations on H_2 , the reference curves are 2 electron, 2 orbital, state averaged CASSCF (6-31G* basis, rigid rotation). As has been pointed out, the single determinantal RHF ground state in Fig. 4a has a cusp at 90° twist. Nevertheless, the RCIS singlet and triplet agree well with the CASSCF curves. Figure 4b shows that the UHF ground state does not have a cusp at 90° (but has high spin contamination). However, the UCIS triplet is qualitatively incorrect - instead of a minimum, it has a barrier at 90° and is degenerate with the excited singlet. Thus UCIS should be avoided for this and related systems.

The twisting of a polar π bond in CH_2NH is shown Figure 5. Because the nitrogen lone pair can participate in bonding as the π bond is rotated, it must be included in the active space of the CASSCF (i.e. 3 orbital, 4 electron). Unlike ethylene, the ground state RHF curve does not have a cusp at 90° due to the lower symmetry and the polarity of the C-N bond. The RHF/UHF instability is also confined to a much smaller range (ca. $80^\circ - 100^\circ$). The RHF ground state and the RCIS singlet have the correct shape but are higher in energy than the corresponding CASSCF curves. Because of the larger active space, the CASSCF calculations include some electron correlation, thus displacing these curves to lower energy. The RCIS triplet has a curious bump near 90° that may merit further study.

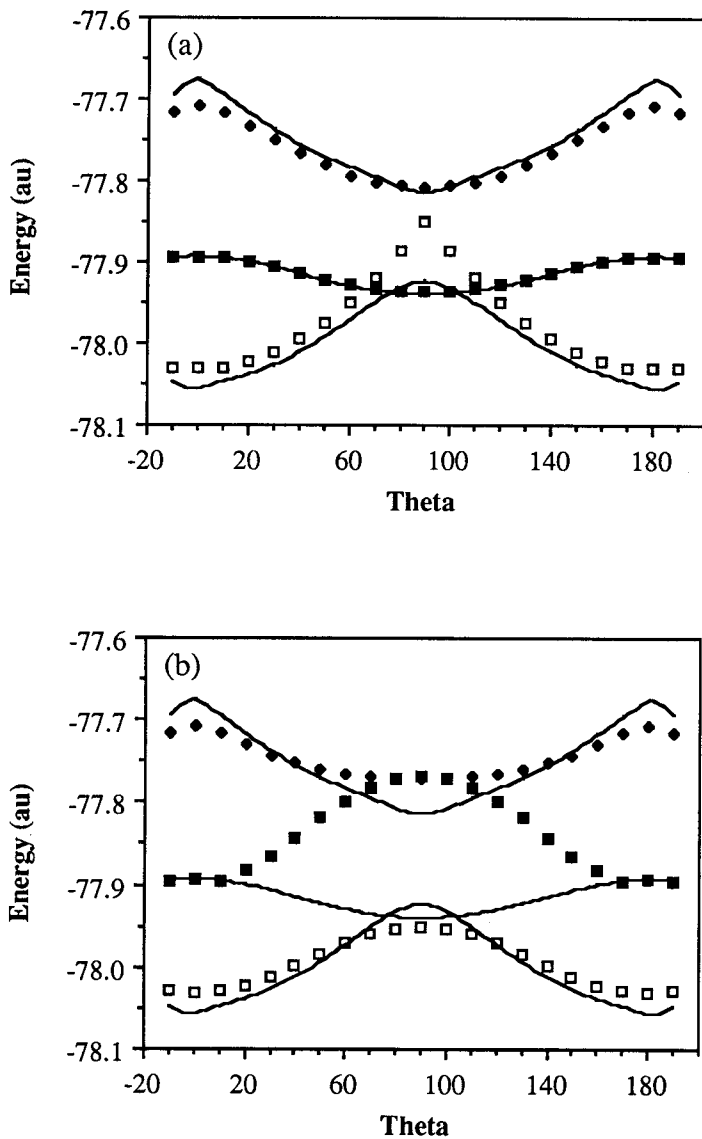


Figure 4. Comparison of CIS and CASSCF potential energy curves for rigid rotation of the π bond in C_2H_4 (a) spin restricted, (b) spin unrestricted (open squares - RHF or UHF ground state, diamonds - RCIS or UCIS singlet, filled squares - RCIS or UCIS triplet, solid lines - 2 electron, 2 orbital state averaged CASSCF).

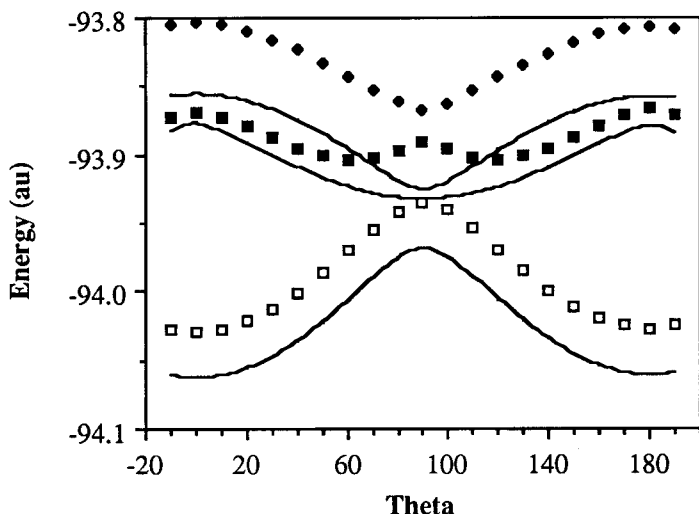


Figure 5. Comparison of spin restricted CIS and CASSCF potential energy curves for rigid rotation of the π bond in CH_2NH (open squares - RHF ground state, diamonds - RCIS singlet, filled squares - RCIS triplet, solid lines - 4 electron, 3 orbital state averaged CASSCF).

To summarize, simple potential energy curves for the lowest excited singlet and triplet states for non-polar systems are represented fairly well by restricted CIS calculations. For polar molecules, the RCIS singlet curves may be qualitatively correct but caution may be needed for some triplets. Unrestricted CIS is not reliable if the ground state has serious spin contamination problems.

6. Conclusions

CI singles is an easy-to-use, systematic method suitable for surveying many excited states of chemical interest. Unlike MC-SCF and MR-CI methods for excited states, CIS can be used in a 'black-box' fashion to give qualitatively correct results for low lying valence states and for Rydberg states. Energies can be improved by second order perturbation theory yielding excitation energies with average errors of 0.5 eV or less, provided diffuse functions are included in the basis set. Direct methods permit CIS to be applied to large systems such as porphyrin.² The availability of analytical gradients for CIS makes it easy to optimize geometries, determine vibrational frequencies and calculate molecular properties of excited states. Spin restricted CIS provides a better description of

excited state potential energy curves than spin unrestricted CIS and may be suitable for some non-polar molecules.

7. References

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