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Selection of Configurations for SCF–CI Calculations of Spectral Properties and Comparison with TDHF Calculations.

I. Convergence to CCI Results in PPP Calculations on $S_o \rightarrow S_x$ Transitions in 6π-Electron Systems

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Comparison is presented of energies, oscillator strengths, and polarization directions calculated using the dipole length and dipole velocity formulas for the lowest 4–7 $\pi\pi^*$ transitions in eight 6π-electron molecules of C_s symmetry using various amounts of CI, from singly excited configurations only (SCI) to complete CI (CCI), and also using the time-dependent Hartree-Fock (TDHF) method. The standard simple PPP approximation was used. For the strongest transitions, SCI and especially TDHF give results in fairly good agreement with CCI. For weaker transitions both SCI and TDHF give similar results, quite different from the CCI solutions. Rational methods for selecting a small number of configurations needed to reproduce correct order of excited states (SECI-1) or a somewhat larger number reproducing correct order, energies, oscillator strengths and polarization directions of transitions (SECI-2) are presented. Both, and particularly the latter, give similar results from both dipole length or dipole velocity formulas when Linderberg's relation is used for matrix elements of the linear momentum operator and in this respect resemble the TDHF and CCI methods for which both formulas necessarily give identical results.

Key words: Transition moment and gradient directions – Selection of configurations – Time-dependent Hartree-Fock.

Introduction

The method of configuration interaction (CI) is one of the commonly used tools for the calculation of molecular spectral properties, such as electronic excitation energies, oscillator strengths (f), polarization directions (ϕ), and quantities characterizing natural and magnetic circular dichroism (CD and MCD, respectively). In principle, given a finite basis of molecular orbitals, one could obtain the best possible wavefunctions by performing complete configuration interaction (CCI). This is rarely feasible, and it is therefore important to find rational ways for truncation of the CI expansion which would still provide results close to the CCI results for the transitions and properties in question [1]. This problem is common to *ab initio* and semiempirical methods, and although

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here we shall limit our attention to one of the latter, we hope that some of the results will be of general interest.

When working with semiempirical methods, one can handle the problem in basically two ways. First, an attempt may be made to find a parameterization which reproduces experimental results while keeping the necessary amount of CI at a minimum: the closed-shell ground state is described by a single ground state SCF configuration and the low-lying excited states by linear combinations of a limited number of singly excited configurations (or possibly of all singly excited configurations, abbreviated SCI in the following). Brillouin's theorem disallows mixing between the ground and singly excited configurations. This program has been remarkably successful for the calculation of ground state properties [2] and some spectral properties [3]. For example, a variety of modifications of the original Pariser-Parr-Pople (PPP) procedure for π-electron systems [4] permit an apparently quite reliable prediction of excitation energies and state symmetries, and order-of-magnitude estimates of oscillator strengths, using only singly excited configurations. Typically, not even all of those are needed. They are usually selected either according to the size of the diagonal element of the Hamiltonian or by limiting the number of orbitals from which and into which excitations are considered. Once 20–40 configurations have been selected, the results for the lowest 5–10 states are rarely changed by the addition of further singly excited configurations, even in the case of sensitive properties such as ϕ's in molecules of low symmetry [5]. The degree of apparent overall success of the SCF-SCI method is remarkable considering that there seems to be little a priori physical reason for it, and since addition of multiply excited configurations is known to affect the results significantly [6–9].

The second approach is to limit all of the empiricism to the form of the parameterized semiempirical Hamiltonian itself and then find its exact eigenfunctions, i.e., to find a parameterization such that the CCI results fit experimental values. This should make it much easier to understand the physical meaning of the parameters and to relate them to observable atomic properties, to compare with other approaches such as valence-bond or multi-configurational SCF, and with *ab initio* methods. This approach need not be meant to replace the far simpler first approach, but rather, to improve the theoretical understanding of why semiempirical models work, and what their scope and limitations are. This line of research was pioneered by Koutecký, Allinger, and their respective collaborators [6–8], and has been taken up by many others since [9]. During this work, a potentially very serious flaw in the simpler SCI approach was discovered: interaction with some doubly excited configurations is so strong that it may change substantially the predicted order of excited states in molecules such as benzene or butadiene. While definitive experimental data are still awaited [10], the general reliability of the SCI results is in question.

Our experimental work on the determination of polarization directions in molecules of low symmetry [5, 11], on magnetic circular dichroism [12], and on electronic spectroscopy of biradicaloid hydrocarbons [13] (those with two almost non-bonding orbitals occupied by a total of only two electrons in the ground state) indicated additional problems with the SCI description and prompted us to perform a more systematic study of extensive CI with multiply excited configurations. The main such problems are:

1. Oscillator strengths, f, and polarization directions, ϕ, are usually obtained from either transition dipole moments or transition dipole gradients. The former are related to matrix elements of the position vector operator $\hat{\boldsymbol{r}}$, the latter to matrix elements of the linear momentum operator $\hat{\boldsymbol{p}}$. For exact wavefunctions, the same values result for f and ϕ using either operator. For approximate wavefunctions, this is not true. Linderberg [14] has shown that in zero-differential-overlap models the proper commutation relation between $\hat{\boldsymbol{r}}$ and $\hat{H}$ can be secured by the use of the following expression for the elements of $\hat{\boldsymbol{p}}$ over atomic orbitals: $\langle\mu|\hat{\boldsymbol{p}}|\nu\rangle = im\beta_{\mu\nu}(\boldsymbol{R}_\nu - \boldsymbol{R}_\mu)/\hbar$. When values of $\langle\mu|\hat{\boldsymbol{p}}|\nu\rangle$ obtained from Linderberg's expression are used, a CCI calculation gives the same results irrespective of whether the $\hat{\boldsymbol{r}}$ or $\hat{\boldsymbol{p}}$ operator is used. On the other hand, this is not so for an SCI calculation [15]. There has been some argument about which operator to use in the latter case [16, 17], but since $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ are both equally justified theoretically [17], one tends to mistrust procedures in which they give different answers.

2. A similar problem occurs in the calculation of B terms in MCD spectra, since the usual perturbation expression [18] involves the elements of dipole length, or dipole velocity, and angular momentum operators. Moreover, each term involves a summation over all excited states and the SCI truncation may be too severe. Finally, CCI results are origin-independent [12], while other truncations lead to origin-dependent results in molecules of low symmetry [19].

3. Biradicaloid hydrocarbons have low-energy doubly excited configurations and their electronic states thus cannot be described well by the SCI scheme. We have recently assigned an observed excited state in such a hydrocarbon as a predominantly doubly excited state [13] and expect that the number of such assignments will increase in the future. Even in "ordinary" hydrocarbons, some experimental assignments indicate significant involvement of doubly excited configurations [10].

4. The SCI scheme can describe singlet as well as triplet states, but a different set of parameters is required in each case to obtain agreement with experiment [20]. This may be due to a different degree of mistreatment of correlation energy in the two cases, and it would be interesting to see whether just one set of parameters could be used in a CCI treatment.

5. Observations of $S_1 \rightarrow S_x$ absorption spectra have been reported recently (for a recent list of references see Ref. [21]). It has been claimed [21] that assignments can be based on SCI calculations, but the argument is not entirely convincing, since the S_x states may well have a significant degree of doubly excited nature. Moreover, the assignments will inevitably rely largely on calculated intensities, and these are probably relatively poorly predicted by SCI.

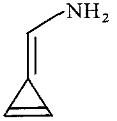
An alternative way to proceed beyond the SCI method, particularly appealing for $S_0 \rightarrow S_x$ transitions, and very little explored, is the time-dependent Hartree-Fock method (TDHF) [22, 23]. Like CCI, it provides identical results from the use of $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ operators [22, 23], and it is computationally much simpler, particularly for large molecules. The computational effort is comparable to that in SCI, and as in SCI, higher singly excited configurations have little importance for the lowest few excited states and may be omitted from the calculation. However, TDHF may run into problems in the case of ground state instabilities and yield imaginary excitation energies [24]. A more systematic investigation of its potential and comparison with CI seems well worthwhile.

Method and Results

While CCI calculations would be ideal, they are usually not feasible, and we have therefore started an investigation of how far beyond SCI one needs to go before the results approximate their CCI values within prescribed limits. We have started our work by investigating $S_0 \rightarrow S_x$ transitions since they are of most immediate experimental interest to us. Almost all previous authors interested in this problem have limited their attention to the energies of the excited states. However, these are not a very sensitive criterion of convergence to CCI results, and our study is based on inspection of not only the values of E, but also those of f and ϕ, the latter two being calculated using both the $\hat{r}$ and $\hat{p}$ operators. After some experimentation, we settled for the following prescribed limits for the deviation from CCI results: correct order and relative energies of the 5–10 lowest energy transitions (depending on the size of the molecules and excepting the order of nearly degenerate transitions), absolute magnitudes of transition energies within 0.5 eV, oscillator strengths within a factor of two, polarization directions within 20°, and agreement between $\hat{r}$ and $\hat{p}$ based values within 50% for oscillator strengths and within 10° for polarization directions. It can be expected that the values of f and ϕ for very weak transitions will approach their CCI values slowly, since they are likely to be affected by even a minor admixture of new configurations into the ground or excited states. These transitions are of experimental importance only if they are not overlapped by much stronger absorptions, i.e., typically, only if there is no strong transition at lower energies. Also, vibronic interactions are likely to intervene and make comparison between experimental and calculated results difficult. We shall be less concerned with cases of limited experimental interest.

Since we are interested in eventual application to our experimental problems, we need a method of generation and selection of configurations applicable to relatively large systems, such as 20 electrons in 20 orbitals. It is crucial to select all of the important configurations and as few as possible of those which are not needed, since otherwise the computation time and storage requirements will be excessive. We have set an arbitrary limit of 200 as the maximum number of configurations to be included. This precludes immediately the use of simple diagonal criterion used by most authors for the choice of configurations, since the cut-off energies would have to be unrealistically small.

After an initial analysis of some 4-electron cases [15], we have selected eight six-electron molecules with no symmetry element other than the molecular plane (I–VIII). The choice was guided by a desire to include a variety of structural



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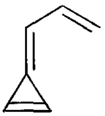
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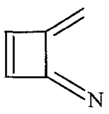

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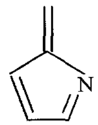

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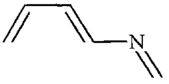

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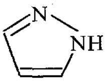

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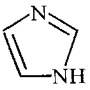

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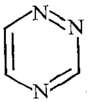

(VIII)

types. For a system of this size the CCI calculation is still fast, and we were thus able to compare truncated CI calculations with the exact CCI results (6 electrons in 6 orbitals give rise to 175 singlet configurations, counting separately linearly independent singlet configurations with identical space part but different spin functions). Calculations using all singly, doubly and triply excited configurations (SDT-CI, 120 in all) give results which differ very little from CCI results, in almost all cases well within our tolerance limits. Calculations on the SDT-CI level are, of course, still impracticable for larger molecules. However, inspection of the wavefunctions indicated that most of the configurations included in the SDT-CI calculations were apparently unnecessary for our purposes.

In the "normal" (as opposed to biradicaloid) molecules I–VIII, the ground state wavefunction $|0\rangle$ resulting from the CCI calculation has a predominant contribution from the ground state configuration G. It can be written as:

$$|0\rangle = C_G G + \sum_i c_S^i S^{0i} + \sum_i C_D^i D_a^{0i} + \sum_i c_D^i D_b^{0i} + \sum_i c_T^i T^{0i} + \sum_i c_Q^i Q^{0i}$$

where the coefficient C_G is very large (~ 0.9), C_D^i's are relatively large (~ 0.1), and c_S^i's, c_D^i's, c_T^i's, and c_Q^i's are small. S^{0i} is the i-th singly excited configuration, D_a^{0i} is the i-th doubly excited configuration among those which are important in the ground state, and D_b^{0i} among those which are not. Similarly, T^{0i} is the i-th triply excited configuration, and Q^{0i} is i-th among more than triply excited configurations. In this context, a configuration is considered important if its coefficient is larger in absolute value than a pre-defined limit. In "biradicaloid" molecules, one of the doubly excited configurations enters $|0\rangle$ with a weight comparable with that of G and the following analysis will not be justified. Although we are interested in such molecules as well, for the time being we limit our attention to the far more common "normal" ones.

Inspection of CCI results also showed that the wavefunctions of low-lying excited states $|I\rangle$ can usually be written as:

$$|I\rangle = k_G^I G + \sum_i K_S^{Ii} S_m^{Ii} + \sum_i k_S^{Ii} S_n^{Ii} + \sum_i K_D^{Ii} D_m^{Ii} + \sum_i k_D^{Ii} D_n^{Ii} + \sum_i k_T^{Ii} T^{Ii} + \sum_i k_Q^{Ii} Q^{Ii},$$

where K_S^{Ii}'s and K_D^{Ii}'s are relatively large (~ 0.5) and all k^{Ii}'s are small (~ 0.2 or less). Here, S_m^{Ii} is the i-th singly excited configuration among those which are important in the state $|I\rangle$, and S_n^{Ii} the i-th among those which are not. Similarly, D_m^{Ii} is the i-th doubly excited configuration among those which are important in the state $|I\rangle$, D_n^{Ii} the i-th among those which are not, and T^{Ii}, Q^{Ii} have a similar meaning as T^{0i}, Q^{0i} did for $|0\rangle$.

Clearly, G and configurations D_a^{0i}, S_m^{gi} and D_m^{gi} for all i and all states $|I\rangle$ which are of interest must be included in the calculation if the correct order and relative energies of states are to be predicted consistently correctly. Since the same configuration can appear several times on this list, we shall refer to sets of configurations G, D_a, S_m, and D_m in the following and assume that all repetition has been eliminated. The number of the lowest excited states which are of interest is determined before the calculation starts. It is relatively easy to select the configurations and form the sets before a CI matrix is set up, though the method is not completely foolproof. G is always included. In small molecules like I–VIII, all possible singly excited configurations are included, since they are likely to occur as S_m^{Ii} for some low-lying excited state $|I\rangle$ of interest. In larger molecules the set S_m is selected upon visual inspection of SCI results. Although such a procedure could be easily automated, we find it useful to check for possible input errors at this stage. Those doubly excited configurations for which $|\langle D|H|G\rangle/(E_D - E_G)| > \varepsilon$ are included since they should appear in D_a (E is the energy of the configuration and ε is a preselected constant). Those for which $|\langle D|H|S\rangle/(E_D - E_S)| > \varepsilon$, where S is any of the already selected singly excited configurations, are also included since they are likely to appear in D_m. Moreover, any doubly excited configuration with energy below a predetermined value δ is also included in the set D_m since it probably introduces a new low-lying excited state even if it mixes with no other configurations. This level of CI will be referred to as SECI-1 (selected configuration interaction, first step). As is discussed in more detail in the following, it provides the correct order of excited states but overestimates excitation energies considerably when compared with CCI. This indicates that it might be possible to bring it into agreement with experiment by suitable parameterization. SECI-1 does not provide results which meet our criterion for f and ϕ. Apparently, even some of the configurations which enter with small coefficients into $|0\rangle$ or one of the $|I\rangle$'s contribute significantly to the calculated values of $\langle 0|\hat{\boldsymbol{p}}|I\rangle$ and $\langle 0|\hat{\boldsymbol{r}}|I\rangle$ from which the f's and ϕ's are obtained.

Concentrating on the $\langle 0|\hat{\boldsymbol{p}}|I\rangle$'s for awhile, substitution for $|0\rangle$ and $|I\rangle$ will give a sum of terms of the types $C_G k_G^I \langle G|\hat{\boldsymbol{p}}|G\rangle\,(=0)$, $C_G K_S^{Ii}\langle G|\hat{\boldsymbol{p}}|S_m^{Ii}\rangle$, $C_G k_S^{Ii}\langle G|\hat{\boldsymbol{p}}|S_n^{Ii}\rangle, \ldots, c_S^i k_G^I \langle S^{0i}|\hat{\boldsymbol{p}}|G\rangle$, $c_S^i K_S^{Ij}\langle S^{0i}|\hat{\boldsymbol{p}}|S_m^{Ij}\rangle$, etc. Each term is a product of three numbers: two coefficients and an integral. Terms with two large coefficients, such as $C_G K_S^{Ii}\langle G|\hat{\boldsymbol{p}}|S_m^{Ii}\rangle$, have already been included since G, D_a^{0i}, S_m^{Ii}, and D_m^{Ii} already are on our list of configurations. We shall now assume that no terms with two small coefficients need be included. We further assume that terms with one large and one small coefficient must be included provided that the integral itself is large, but not if it is small. The terms of this kind are $C_G k_S^{Ii}\langle G|\hat{\boldsymbol{p}}|S_n^{Ii}\rangle$, $c_S^i K_S^{Ij}\langle S^{0i}|\hat{\boldsymbol{p}}|S_m^{Ij}\rangle$, $c_S^i K_D^{Ij}\langle S^{0i}|\hat{\boldsymbol{p}}|D_m^{Ij}\rangle$, $C_D^i k_S^{Ij}\langle D_a^{0i}|\hat{\boldsymbol{p}}|S_n^{Ij}\rangle$, $C_D^i k_D^{Ij}\langle D_a^{0i}|\hat{\boldsymbol{p}}|D_n^{Ij}\rangle$, $C_D^i k_T^{Ij}\langle D_a^{0i}|\hat{\boldsymbol{p}}|T^{Ij}\rangle$, $c_D^i K_S^{Ij}\langle D_b^{0i}|\hat{\boldsymbol{p}}|S_m^{Ij}\rangle$, $c_D^i K_D^{Ij}\langle D_b^{0i}|\hat{\boldsymbol{p}}|D_m^{Ij}\rangle$, $c_T^i K_D^{Ij}\langle T^{0i}|\hat{\boldsymbol{p}}|D_m^{Ij}\rangle$. Note that the absence of any terms involving "Q" configurations from this list is consistent with our observation that SDT-CI and CCI give practically identical results for low energy transitions.

In order to include all of the required configurations on our list, the program first generates all singly excited configurations S which are not yet on the list and checks the magnitude of the integrals $\langle G|\hat{\boldsymbol{p}}|S\rangle$, $\langle D_a|\hat{\boldsymbol{p}}|S\rangle$, $\langle S_m|\hat{\boldsymbol{p}}|S\rangle$ and $\langle D_m|\hat{\boldsymbol{p}}|S\rangle$ for all members of the sets G, D_a, S_m and D_m. If any of the integrals of $\hat{p}_x$ and $\hat{p}_y$ are larger than predetermined constants p_{cx} and p_{cy}, respectively, for a given configuration S, then that configuration is added to the list. In small molecules such as I–VIII it is much faster and, as noted above, essentially the same, just to include all singly excited configurations, but the selection procedure becomes important in larger molecules.

Second, the program generates all doubly excited configurations D which are not included in the sets D_a and D_m and checks the magnitude of the integrals $\langle D_a|\hat{\boldsymbol{p}}|D\rangle$, $\langle S_m|\hat{\boldsymbol{p}}|D\rangle$, and $\langle D_m|\hat{\boldsymbol{p}}|D\rangle$ for all members of the sets D_a, S_m and D_m.

The same cutoff values p_{cx} and p_{cy} are used to determine if the configuration D should be included or not.

Third, the program goes through the list of doubly excited configurations included in D_a and D_m and generates all triply excited configurations T which do not differ from these doubly excited configurations by more than one spin-orbital. These are the only ones for which a one-electron operator, such as $\hat{\boldsymbol{p}}$, can have non-zero elements. The magnitude of the integrals $\langle D_a | \hat{\boldsymbol{p}} | T \rangle$ and $\langle D_m | \hat{\boldsymbol{p}} | T \rangle$ is checked against p_{cx} and p_{cy}, and the configurations T are added to the list or rejected accordingly.

The four empirical values which specify cut-off points for selection of configurations, ε, δ, p_{cx} and p_{cy}, were adjusted by measuring the degree of convergence as defined by the adopted limits, while holding the number of configurations to a minimum. A suitable value of ε, as obtained by trial and error, is 0.08–0.1. The value of δ has been set at 7 eV. Of the various possibilities for the choice of p_{cx} and p_{cy}, we have selected one which appears to give the same relative error in the x and y components of the calculated transition gradients[1]. We take $p_{cx} = (k\beta/N) \sum_{\text{bonds}} |B_x|$, $p_{cy} = (k\beta/N) \sum_{\text{bonds}} |B_y|$, where N is the number of atoms, and B_x, B_y are the x and y projections of the bonds in Å units. A suitable value of k was found to be 0.5.

As discussed below, the results of calculations using this extent of CI (SECI-2) satisfy our criteria for approximation to CCI. In particular, the $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ based results are virtually identical, so that it is not necessary to use the matrix elements of $\hat{\boldsymbol{r}}$ in addition to those of $\hat{\boldsymbol{p}}$ for selection of configurations.

The outlined method for selection of configurations may appear cumbersome, but it can be efficiently programmed. On a Univac 1108 Computer with 190K fast memory, a CCI calculation on II (175 configurations) took 184 seconds, while the SECI-2 calculation (48 configurations) took 18 seconds. The savings become even more significant as the size of the molecule increases. A CCI calculation on a 10-electron-10-orbital system is well beyond our means, but a SECI-2 calculation on azulene (102 configurations in all) took only 145 seconds. The computation times quoted include the initial SCF iterations, the selection of configurations, the calculation of the CI wavefunction, of density matrices for the eight lowest excited states, and of transition density matrices, f, and ϕ for transitions from the ground state to these eight states, using both the $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ methods.

We have also investigated the effect of the choice of parameters for carbon on the results. Variation of the resonance integral $\beta(-2.1$ or -2.318 eV) and of the one-center electron repulsion integral γ_{C} (9.5 or 10.72 eV) does not affect

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[1] We need a rough estimate of how the matrix elements of $\hat{p}_x$ and $\hat{p}_y$ depend on molecular geometry. In atomic units, $\boldsymbol{P}_{AB} = \langle A | \hat{\boldsymbol{p}} | B \rangle = K_K \sum_l \sum_m U_{rl} U_{sm} (\boldsymbol{R}_m - \boldsymbol{R}_l) \beta_{lm}$, where A and B are configurations with mismatch in orbitals r and s, K_K is the corresponding Sanibel coefficient, U_{rl} is the coefficient of the r-th molecular orbital at the l-th atom, and R_m is the position vector of the m-th atom. A rearrangement of terms gives $\boldsymbol{P}_{AB} = \mathrm{K}_K \sum\sum_{l<m} [U_{rl} U_{sm} - U_{rm} U_{sl}] (\boldsymbol{R}_m - \boldsymbol{R}_l) \beta_{lm}$. Very roughly, $|U_{pq}|$ has the order of magnitude of $1/\sqrt{N}$. Making this substitution the bracketed terms will vanish or equal $\pm 2/N$. Using $1/N$ as fairly representative, ignoring the Sanibel coefficient, assuming that β is the same for all bonds, and that moreover all bonds contribute to the sum with the same sign, $(P_{AB})_x = (\beta/N) \Sigma |B_x|$, and similarly for the y component.

the degree of convergence of the SECI-2 results to CCI results. As expected [7], use of the Ohno-Klopman functional form [25] for the electron-repulsion integrals as a function of distance gives results which approach the CCI limit somewhat faster than those obtained with the Nishimoto-Mataga formula [26]. This is seen on both SDT-CI and SECI-2 results. The bulk of our results (including those in Figs. 1–6) were obtained with the Ohno-Klopman formula, using all bond lengths equal to 1.40 Å and parameter values suggested in Ref. [7, 27]. ($IP_C = 11.42$ eV, $\gamma_C = 10.84$ eV, $IP_{N(aza)} = 16.55$ eV, $\gamma_{N(aza)} = 14.77$ eV, $IP_{N(pyrrole)} = 24.0$ eV, $\gamma_{N(pyrrole)} = 16.0$ eV, $IP_{N(amine)} = 25.4$ eV, $\gamma_{N(amine)} = 16.5$ eV, $\beta_{CC} = \beta_{CN} = \beta_{NN} = -2.318$ eV). Regular polygon geometries were used.

The TDHF results were obtained in the usual way [22], using the same parameters and geometry as in the CI calculations.

Discussion

We have obtained results for energies, oscillator strengths, and polarization directions of $S_0 \rightarrow S_x$ transitions in molecules I–VIII by SCI, SD-CI, SECI-1, SECI-2, SDT-CI and TDHF methods, using both $\hat{r}$ and $\hat{p}$ operators, and compared them with CCI results. In order to trace a state through the SCI, SD-CI, ..., CCI series of calculations, we have evaluated the overlap of the approximate wavefunctions with the exact CCI result. Some relatively low-lying states obtained from CCI cannot be identified with any SCI or TDHF states, since they are predominantly of multiply excited character. Identification of CCI results with TDHF results was done by comparison of TDHF with SCI. In the following, the individual approximate methods are compared to the exact CCI solutions. Of course, it will be remembered that the CCI solutions need not agree with experiment, particularly in semiempirical methods.

The SCI and TDHF methods give quite similar results. They correctly represent the lowest two transitions, overestimating their energies somewhat, but the order of the higher transitions is frequently wrong and some are usually missing. The composition of the wavefunctions of the higher states is often totally unrelated to the CCI wavefunctions (overlaps of the order of 0.3). Also f and ϕ for the strongest transitions are well predicted by TDHF (f within 20%, ϕ within 15°) and by SCI. The two results for f in the latter method often differ by a factor of 2, but the mean value of the dipole length and dipole velocity results is usually very close to the TDHF result. One exception is molecule II where transition 6 is predicted correctly by TDHF but where SCI gives errors larger than expected both in f and ϕ.

For the weaker transitions the oscillator strengths in SCI and TDHF are often off by an order of magnitude in either direction, and large errors are also found in the results for ϕ. In such cases the disagreement between $\hat{r}$ and $\hat{p}$ based values in SCI calculations is only a minor inconvenience. They are usually within a factor of 2 although they can differ more for very weak transitions, and either one can be closer to the correct value. The situation is somewhat better for polarization directions. The values obtained with $\hat{r}$ and $\hat{p}$ operators are identical for TDHF and within less than 10° for SCI. However, their absolute values are approximately correct (error less than 20°) only for transitions with f_{SCI} above about 0.1.

SECI-1, SECI-2 and SD-CI are essentially equivalent with respect to energy ordering of states. All of these methods failed to predict the order of a pair of states in only two cases. The first case (states 3 and 4 of II) is characterized by a near degeneracy (~0.02 eV energy difference) of the corresponding CCI states, while the second (states 4 and 5 of VI) involves states of quite high energy (7.5 and 8.0 eV at CCI).

SECI-2 and SD-CI are about equally successful in predicting transition moment directions except in rare cases such as state 3 of II where there is a large difference in angle between CCI and SDT-CI. SECI-1 is erratic in its prediction of transition moment directions of weak transitions, but performs well for strong ones. For oscillator strengths, SECI-2 is better than SD which is in turn slightly better than SECI-1.

The results of SECI-2 calculations using cutoff values for ε, δ, p_{cx} and p_{cy} as specified above give results for E, f, and ϕ within the desired limits of error.

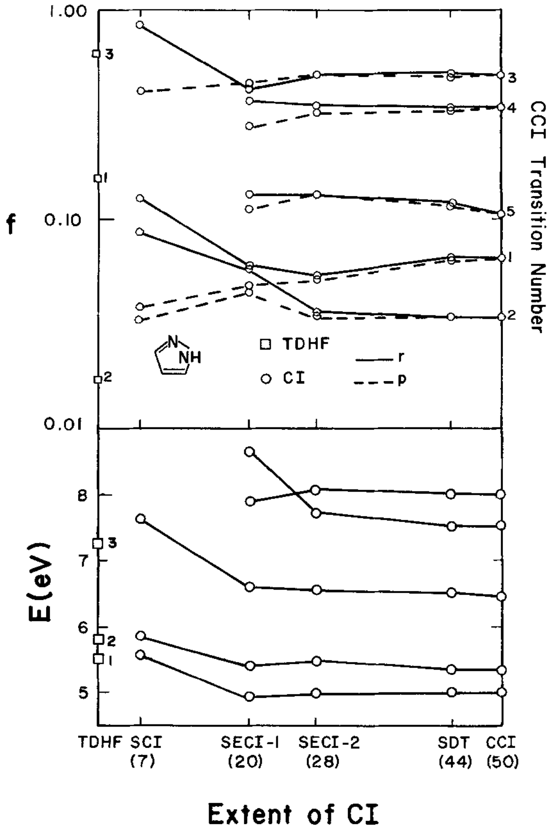
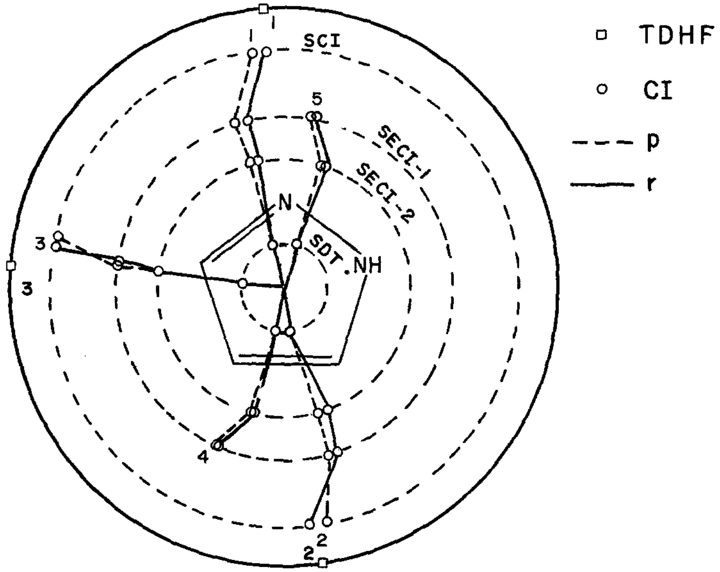
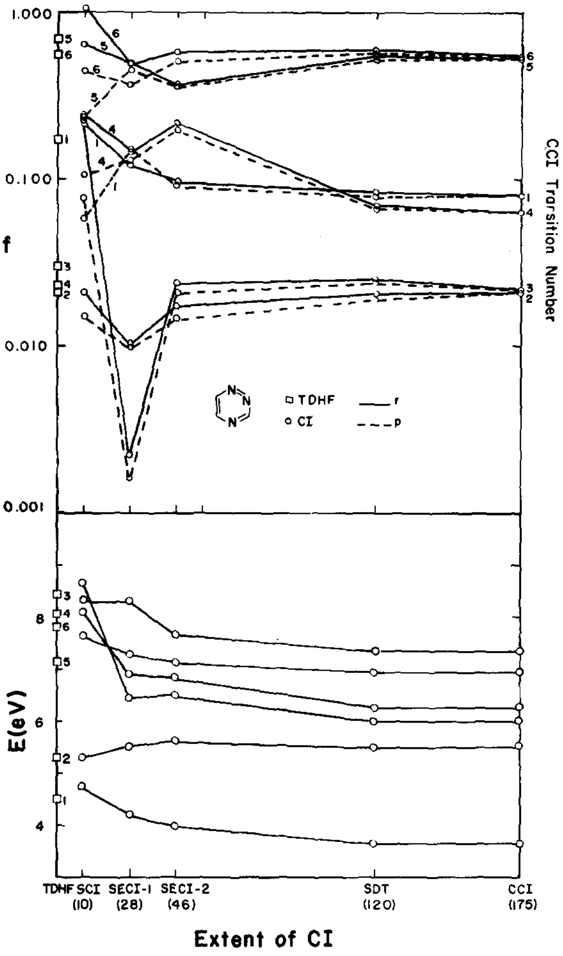


Fig. 1. Results for VI: excitation energies (bottom) and oscillator strengths [top, using dipole length (r) and dipole velocity (p) formulations] as a function of the number of configurations (in parentheses) used in the CI procedure. For abbreviations of configuration selection methods, see text. On the left, time-dependent Hartree-Fock results. State numbering is in the order of CCI energies. One-to-one correspondence is assumed between TDHF and SCI states



TDHF
CI
p
r
SCI
SECI-1
SECI-2
SDT
N
NH
5
3
3
4
2
2

Fig. 2



1.000
0.100
0.010
0.001
f
E(eV)
8
6
4
CCI Transition Number
1
2
3
4
5
6
TDHF
CI
r
p
N
TDHF SCI (10)
SECI-1 (28)
SECI-2 (46)
SDT (120)
CCI (175)
Extent of CI

Fig. 3

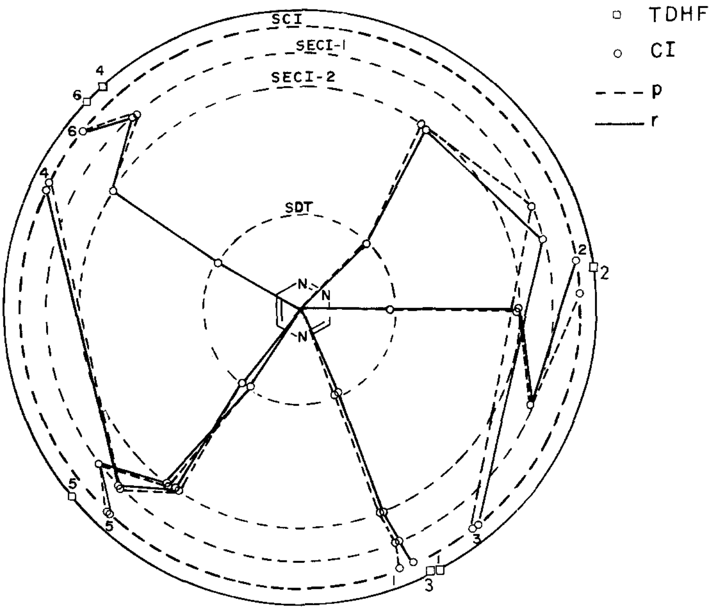


Fig. 4. Results for VIII; see caption to Fig. 2

Only the values of *f* and ϕ for transitions into a few weak predominantly doubly excited states in II and III exceed the error limits. Perhaps significantly, these are the only cases in which the $\hat{r}$ and $\hat{p}$ based values disagree by more than a factor of 1.2–1.5.

The results of SDT-CI calculations are virtually identical to CCI results in all respects. The only exceptions occur for *f* and ϕ values for very few of the above-mentioned cases of predominantly doubly excited states (in II and III).

Results shown in Figs. 1–6 have been selected to illustrate representative cases. For a typical well-behaved molecule (VI, Figs. 1, 2) convergence to CCI results is fast. Nevertheless, some of the higher energy states are described poorly or are missing altogether in the SCI calculation. An average-behaved molecule is represented by VIII (Figs. 3, 4). SCI predicts wrong order of states except for the lowest two and is of little use for prediction of polarization directions except for the strongest transitions. The order of energies is corrected by going to SECI-1; the angles require going to SECI-2. The worst-behaved molecules

Fig. 2. Results for VI: Transition moment directions (full, from dipole length; dashed, from dipole velocity formula) plotted with respect to molecular framework shown in center, as a function of the number of configurations (radial distance from perimeter) used in the CI procedure. Points for CCI are not shown; the directions are indicated as tangents at the origin. For abbreviations of configuration selection methods, see text. On the perimeter, time-dependent Hartree-Fock results. State numbering is in the order of CCI energies. One-to-one correspondence is assumed between TDHF and SCI states

Fig. 3. Results for VIII; see caption to Fig. 1. TDHF states 4 and 6 apparently correspond to SCI states 6 and 4, respectively

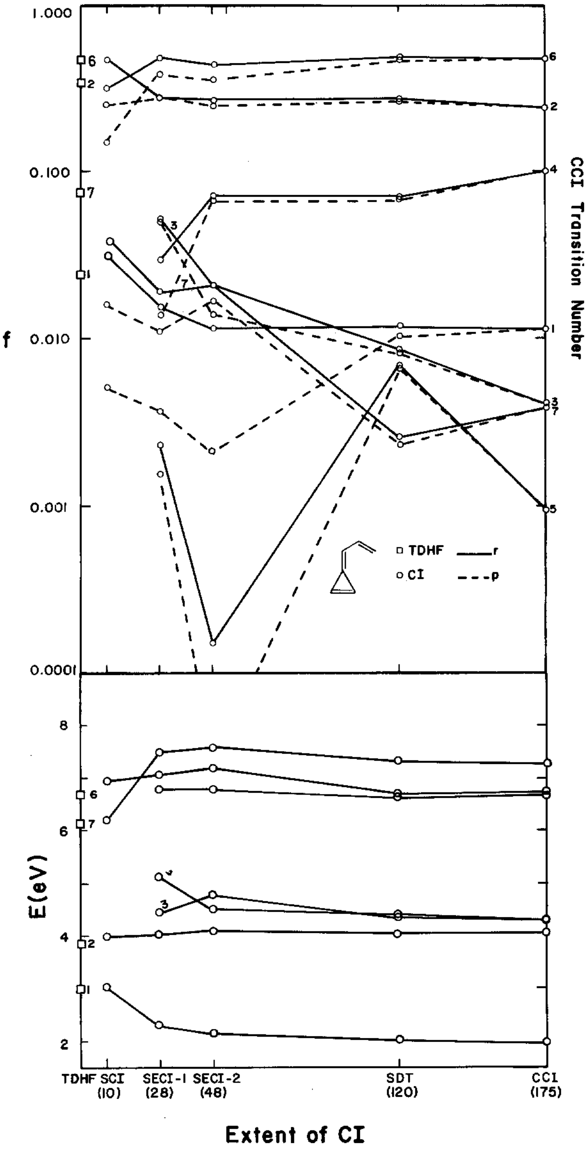


Fig. 5. Results for II; see caption to Fig. 1

of the set are II (Figs. 5, 6) and III. Indeed, the CCI wavefunctions of some of their low-lying excited states have large contributions from doubly and even triply excited configurations, and SDT-CI results for f and ϕ are still not converged to CCI results for the weaker of the transitions. SCI results for f and ϕ are essentially worthless, SECI-1, SECI-2, and SD (not shown in the Figures) fail for the weak and even some of the strong transitions. Thus, although SECI-1 and SECI-2 clearly are superior to the usual SCI approach, they are not foolproof. It is not clear at present how to tell whether they will work for any given

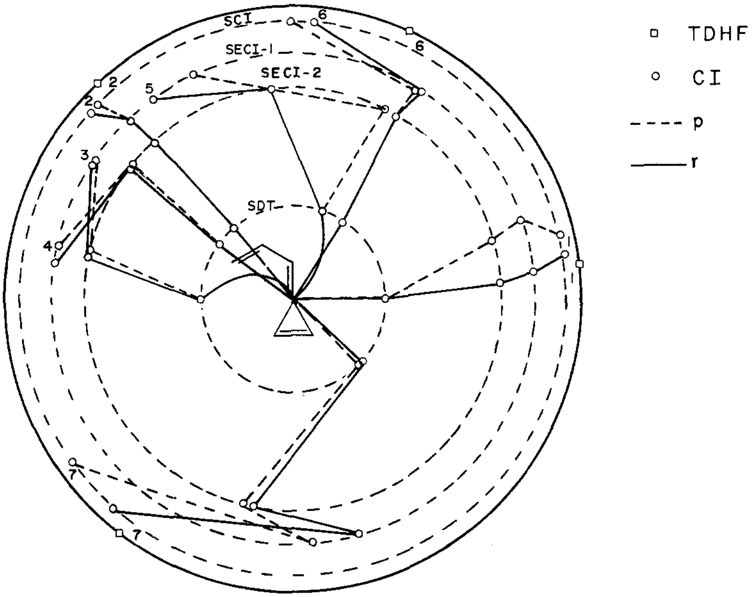


Fig. 6. Results for II; see caption to Fig. 2

molecule, except that the occurrence of discrepancies between $\hat{r}$ and $\hat{p}$ based values at the SECI-2 level is a clear warning of danger.

The small molecules I–VIII selected for the present study are well-suited for an investigation of convergence to CCI results, since CCI calculations are easily performed on them. The extent to which our conclusions remain valid for larger molecules will be hard to estimate. We plan to investigate the quality of SECI-2 results indirectly, by looking for disagreement between $\hat{r}$ and $\hat{p}$ based values, and for changes upon inclusion of additional configurations.

The ultimate test of the meaningfulness of our results will be comparison with experiment. However, this depends not only on the quality of the solution of the Schrödinger equation for the model Hamiltonian, but also on the appropriateness of the Hamiltonian itself. Molecules I–VIII are not particularly useful for comparison with experiment, and such comparison is not the aim of this paper. Deeper concern with the adequacy of the model Hamiltonian, in particular the π-electron approximation, ZDO approximation (and related neglects in the evaluation of matrix elements of $\hat{r}$ and $\hat{p}$), and choice of parameters for carbon and heteroatoms will be legitimate when comparison with experiment is attempted. We plan to address ourselves to those problems but only after we have in hand a well-defined and effective procedure for selection of configurations.

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