Comparison of INDO and *ab Initio* Methods for the Correlated Wave Functions of the Ground and Excited States of Ozone

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Abstract: The validity of using integral approximation schemes in conjunction with correlated wave functions has been tested by performing generalized valence bond (GVB) and extensive configuration interaction (CI) calculations with INDO approximate integrals on the ground and excited states of ozone. High quality *ab initio* calculations have previously shown correlation effects to be extremely important for describing ozone. We find that for the CI wave functions the INDO approximation leads to vertical excitation energies within about 30% (from 0.8 eV too low to 0.6 eV too high with an RMS error of 0.5 eV), as compared to comparable *ab initio* calculations. We also found that the INDO–GVB wave functions lead to bond angles in good agreement with experimental and *ab initio* calculations but produced bond lengths that were too short. Most important was the discovery that INDO grossly favors closed geometries as opposed to open geometries, predicting the ground state of ozone to be an equilateral triangle state (even for correlated wave functions) with an energy 6 eV below the correct open state!

In recent years significant progress has been made in developing efficient procedures for carrying out high quality *ab initio* calculations.[3,4] Extensive configuration interaction (CI) calculations with large basis sets have been reported for the ground and excited states of molecules such as C_2H_4,[5] C_4H_6,[6,7] C_6H_6,[8] O_3,[9] CO_2,[10] etc., and for ground state potential surfaces of reactions such as[11-13] $LiH + H \rightarrow Li + H_2$, $H_2 + F \rightarrow H + HF$, $F_2 + H \rightarrow F + HF$. Despite this progress, we have a long way to go before such *ab initio* methods will be efficient enough (in both computer time and people time) for thorough mechanistic investigations of chemically interesting reactions (involving, perhaps, hundreds or thousands of geometries).

To circumvent the feasibility restrictions of *ab initio* procedures, a number of approximate methods for calculating wave functions have been developed. Most of these approximations involve some empiricism, *i.e.*, parametric fitting of experiment. Moreover, essentially all the semiempirical methods are based upon closed-shell Hartree–Fock (HF) wave functions, including (i) noninterative approaches such as extended Hückel theory (EHT),[14] (ii) self-consistent charge generalizations of EHT,[15] (iii) CNDO,[16] (iv) INDO[17] and MINDO,[18] (v) NDDO,[19] (vi) noniterative simple pseudopotential approaches (commonly used for solids),[20] (vii) Xα-type approaches (commonly used for solids).[21] (The CNDO, INDO, and Xα methods have also been used with unrestricted HF wave functions, which allows the lowest state of each spin to be treated approximately.) It is well known that simple HF wave functions (even when carried out exactly) generally lead to poor descriptions of the relative ordering of molecular excited states. For example, the ground states of C_2 and O_3 are known[22,23] to be singlet states, but in each case the HF wave functions leads to a triplet ground state.[9b,24-28] Even worse are the descriptions HF wave functions usually give for potential surfaces involving bond formation or breakage.[29,30] This is unfortunate since it is just in the study of such excited states and reactions that reliable theoretical wave functions are so greatly needed. Consequently, in studying

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[25] The HF wave function also leads to a triplet ground state for BeO,[26] while good CI calculations lead to a singlet state.[27] Although there is no definitive experimental evidence for a ground singlet state,[28] correlations between theoretical calculations and the available experiments point strongly toward a ground singlet state.

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[30] These problems of the HF wave function do not depend on whether an *ab initio* or an approximate method is employed.

Table I. Vertical Excitation Energies of Ozone (Electron Volts)[a]

	HF		GVB(1)			MBS–CI[b]				DZ–CI[c]	
		Ab initio		*Ab initio*		No. of	No. of		*Ab*	*Ab*	
	INDO–MBS	DZ[d]	INDO–MBS	MBS[e]	DZ[d]	DET	SEF	INDO	*initio*[e]	*initio*	Exptl[j]
$^1A_1(4\pi)$	0.00	0.00	0.00	0.00	0.00	197	92	0.00	0.00	0.00	
$^3B_2(4\pi)$	−2.24	−2.16	0.51	0.51	0.68	155	114	0.89	1.11	1.47	
$^3B_1(5\pi)$		0.58	0.88[f]	1.04[f]	1.23[f]	247	186	2.66	2.02	1.74	
$^3A_2(5\pi)$	0.94	0.79				247	186	2.37	1.79	1.80	
$^1A_2(5\pi)$		1.25	0.95[f]	1.15[f]	1.34[f]	382	135	2.54	1.96	1.98	
$^1B_1(5\pi)$		1.42				382	135	2.83	2.24	2.06	2.05–2.15
$^3B_2(6\pi)$	−1.09	−0.52	1.66	2.09	2.33	138	106	2.47	3.20	3.86	
$^1A_1(6\pi)$	4.54	3.72	1.80	2.26	2.51	191	92	2.67	3.50	4.18	
$^1B_2(4\pi)$	4.37	3.85	7.12	8.05	6.70	366	122	7.88	6.70	5.60	4.86
Ring											
$^1A_1(6\pi)$	−6.08[g]	0.36[h]	−6.74[g]	0.15[i]	1.50[h]					1.57	

[a] Ground state experimental geometry employed unless otherwise noted. [b] All single and double excitations (within the GVB(3/PP) space) from dominant configurations. (Two configurations except for $^3B_2(4\pi)$ and $^3B_2(6\pi)$.) [c] DZ (double ζ basis) CI results from ref 9c. A brief description is included in section Ib. *N.b.*, excitations were allowed from 2s-like orbitals. [d] DZ *ab initio* results from ref 9b. [e] MBS (minimum basis set) results from ref 9a. [f] Symmetry was not imposed in these calculations, since a lower energy is obtained for unsymmetric wave functions. [g] Bond angle = 60°. Bond length = 1.255 Å (optimal bond length for INDO GVB (1)). [h] Bond angle = 60°. Bond length = 1.458 Å (optimal bond length for DZ GVB(1)). [i] Bond angle = 60°. Bond length = 1.433 Å (optimal bond length for MBS GVB(1)). [j] Reference 41.

such systems we must expect to use wave functions which contain the electron correlation or many-body effects responsible for the improper behavior of the HF wave functions.

Since semiempirical methods have been developed and used only in conjunction with HF wave functions, there is little information on the appropriateness of approximate methods for correlated wave functions. To elucidate this situation we have used the INDO approximation of molecular integrals to calculate correlated wave functions for the excited states of ozone and have compared these results with those from comparable *ab initio* calculations. INDO appeared to be the most suitable semiempirical approach to test as it was designed and parameterized to fit minimal basis set *ab initio* HF wave functions. In addition, INDO is one of the most popular and successful of the approximate methods, but more important is that INDO often distinguishes correctly between singlet and triplet states and generally yields reasonably good geometries for closed-shell molecules.[31] For example, INDO yields the proper ordering and separation between the $^1A_1$ and $^3B_1$ states of CH_2 and leads to good values for the bond angles.[32]

Ozone was selected, as the test case, since recent *ab initio* calculations[9] have shown it to be particularly poorly treated by HF wave functions; *i.e.*, the many-body corrections are large. A summary of the *ab initio* results on ozone is presented in the next section for convenience of discussion.

I. Preliminaries

A. Summary of *ab Initio* Results for Ozone. *Ab initio* calculations have been performed on the excited states of ozone using the Hartree–Fock (HF), generalized valence bond (GVB), and configuration interaction (CI) methods in conjunction with both minimal basis sets[9a] (MBS) and extended basis sets[9b,c] (specifically, double ζ (DZ) basis sets[33]). Nine low-lying states (<7 eV for the ground state equilibrium geometry) were found. Of these, the first eight states (all <4 eV) involve essentially covalently bonded wave functions that can be well described by taking three ground state oxygen atoms and pairing the atomic orbitals in various ways to form bonds. These states, in turn, can be grouped into three types of configurations according to the number of π electrons, *i.e.*, the number of electrons in orbitals antisymmetric to the molecular plane.[34]

4π: $^1A_1$ (ground state), $^3B_2$

5π: $^3A_2$, $^1A_2$, $^3B_1$, $^1B_1$

6π: 2^1A_1, 2^3B_2

The remaining low-lying state, $^1B_2(4\pi)$, has a large amount of ionic character. The calculated vertical excitation energies for these states are listed in Table I.

The *ab initio* calculations[9] showed that the $^1A_1(6\pi)$ state of ozone has an equilibrium bond angle of 60°. Using the DZ basis, this ring state was found[9c] to be about 1.5 eV above the $^1A_1(4\pi)$ ground state. However, with the MBS, the ring state, $^1A_1(6\pi)$, was found to be nearly degenerate with the $^1A_1(4\pi)$ state.[9a]

Finally, *ab initio* HF calculations[9b] lead to a *triplet* ground state with the singlet state 2.2 eV higher (vertical excitation energy)! The CI calculations, on the other hand, lead to a singlet ground state with the first triplet state at 1.11 and 1.47 eV (vertical excitation energy) for MBS and DZ, respectively. Thus, the correlation errors in the HF description are quite large (3 eV for the $1a_2$ pair) and differ greatly from state to state. This makes ozone an excellent case for testing the validity of the INDO approximation for correlated wave functions.

B. GVB and CI Calculations. The major weakness

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[31] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

[32] W. R. Wadt and W. A. Goddard III, to be submitted for publication.

[33] T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).

[34] The GVB description of the 5π states involves two degenerate configurations corresponding essentially to n → π promotions, *i.e.*, an excitation from a $2p\sigma$ lone pair to a π orbital, on the left or right terminal oxygen atoms. This wave function has C_s rather than C_{2v} symmetry. Expressing the GVB orbitals in terms of symmetry orbitals leads to four dominant configurations, two of A_2 symmetry and two of B_1 symmetry. These are just the dominant configurations in the CI wave function. However, in the HF description, only one such C_{2v} configuration is used. As a result the HF energy of the 5π states is high by about 2.75 eV.

[35] A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **220**, 446 (1953).

of the restricted HF wave function is that the orbitals are forced to be doubly occupied. This restriction is reasonable for inner core orbitals but usually not for the orbitals involved in bonds (*vide infra*). In the GVB method, the double-occupancy restriction is relaxed, replacing the doubly occupied orbital with a pair of singly occupied nonorthogonal singlet-coupled orbitals.

$$\text{HF: } [\phi^{HF}(1)\phi^{HF}(2)] \tag{1a}$$

$$\text{GVB: } [\phi_a^{GVB}(1)\phi_b^{GVB}(2) + \phi_b^{GVB}(1)_a^{GVB}(2)] \tag{1b}$$

For purposes of calculation and comparison, these GVB orbitals, ϕ_a and ϕ_b, are expressed in terms of natural orbitals, ϕ_1 and ϕ_2, so that (1b) becomes[35]

$$\phi_a(1)\phi_b(2) + \phi_b(1)\phi_a(2) = C_1{}^2\phi_1(1)\phi_1(2) - C_2{}^2\phi_2(1)\phi_2(2) \tag{2}$$

Generally, the first natural orbital, ϕ_1, corresponds closely to the HF orbital, ϕ^{HF} (or to a linear combination of HF orbitals).

The simplest form of the GVB wave function consists of an antisymmetrized product of singlet pairs (as in (2)) with the appropriate product of spin functions

$$\mathcal{A}[(\phi_a\phi_b + \phi_b\phi_a)(\phi_c\phi_d + \phi_d\phi_c)\ldots\alpha\beta\alpha\beta\ldots] \tag{3}$$

This is referred to as the perfect pairing GVB wave function[36] and is denoted by GVB(PP), to distinguish it from the more general GVB wave function in which the spin function in (3) is allowed to be completely general (*i.e.*, optimized).[37,38] Since double excitations are well known to be the most important in correlating HF wave functions, we see from (2) and (3) that the GVB-(PP) wave function includes the most crucial of these (along with important higher order terms). The more general spin coupling of the GVB wave function allows certain correlation terms (including some double excitations) that are important in some states of ozone.

The 1s orbitals of the oxygen atom hardly change upon bond formation. As a result, the correlation errors in the 1s pair are expected to be independent of geometry and the same for all (low-lying) excited states. In such cases, the pairs in (3) are *not* correlated but rather are taken as in (1a) instead of (1b). For ozone, the only three pairs that are important to correlate are those that dissociate to singly occupied oxygen atom orbitals as the molecule is pulled apart.[39] Such a wave function is denoted as GVB(3), indicating that all orbitals are doubly occupied except for three pairs (referred to as the GVB split pairs). Of course, *all* orbitals are solved for self-consistently.

After solving for the GVB(3/PP) wave function, we carried out CI calculations using the GVB orbitals (in natural orbital form) just as in the *ab initio* studies. Orbitals from the GVB(3/PP) wave function of the ground state, $^1A_1(4\pi)$, were employed for the 4π and 5π states, while orbitals from the GVB(3/PP) wave function of the $^1A_1(6\pi)$ state were employed for the 6π states. In these calculations the experimental geometry was used (R_{OO} = 1.278 Å, θ = 116.8°[41]). The CI consisted of all single and double excitations from the dominant configurations (two configurations except for the $^3B_2(4\pi)$ and $^3B_2(6\pi)$ states, each of which has only one dominant configuration) but restricting the 1s-like and 2s-like orbitals to remain doubly occupied.

In comparing the results of *ab initio* and INDO–MBS calculations, it is relevant to compare both results with the exact answers in order to determine how important the INDO errors are relative to the error intrinsic to the use of minimum basis sets. Unfortunately, experimental vertical excitation energies are known for only two of the eight transitions under consideration. Consequently, we must use the results of much more extensive calculations as reference standards. Using a DZ basis, Hay, Dunning, and Goddard[9c] have carried out extensive CI calculations on each of the nine states of interest here. Their approach was to (i) solve for the GVB(3/PP) wave function for the ground state and (ii) include all single and double excitations from the dominant configurations with the restrictions that (iii) the 1s-like orbitals were kept doubly occupied and (iv) configurations involving two non-GVB orbitals were deleted. Such calculations are expected to yield vertical excitation energies to within 0.1 or 0.2 eV for valence excited states. (See, for example, the results of Winter, *et al.*,[10] on CO_2.)

Since the GVB orbitals are optimized in terms of their ability to include correlation effects, *moderate* size CI wave functions are equivalent to performing a nearly complete CI in the usual HF basis of occupied and virtual orbitals. (As an example, for the $^1A_1(4\pi)$ state the CI involved 92 spin eigenfunctions (SEF) or 197 determinants; a full CI would involve 207, 025 determinants.) This GVB–CI wave function is similar to what would be obtained by using Bender and Schaefer's iterative natural orbital first-order CI wave function method.[42]

Two of the GVB split pairs correspond to OO σ bonding pairs and are found to be similar for all nine lower states. The third pair, however, changes drastically from state to state. Consequently, a good qualitative description of the excited states if obtained with the GVB(1) wave function. We have also compared the results of *ab initio* and INDO approximations using this simpler description.

In this case we find that the $^1A_1(4\pi)$ state involves

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(36) The methods used to calculate the GVB(PP) wave function (discussed in ref 4) impose orthogonality between orbitals of different pairs. This restriction, known as strong orthogonality, is not important in ozone.

(37) The spin function may be optimized simultaneously with the orbitals, as in the SOGI method[38] (where strong orthogonality is not imposed), or after the orbitals have been optimized, by performing a limited CI on the space spanned by the GVB(PP) orbitals, using just those configurations that will optimize spin. The latter method was employed in the *ab initio* DZ calculations on ozone.[9b]

(38) (a) R. C. Ladner and W. A. Goddard III, *J. Chem. Phys.*, **51**, 1073 (1969); (b) W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971).

(39) In the DZ basis, there is enough flexibility to split the lone pair orbitals on the outer oxygens. Splitting the $2p\sigma$ lone pair orbitals would lead to a more consistent description (with respect to electron correlation) of the vertical excitation energies to the 5π states, as they involve an $n \rightarrow \pi$ promotion. Since the lone pair orbitals in a DZ basis are very similar to simple oxygen 2p orbitals, one would expect the correlation energy of the two orbitals to be about the same. DZ–GVB-(2/PP) calculations on oxygen atoms give an energy lowering of 0.24 eV when the doubly occupied 2p orbital is split.[40] Hence, the tabulated *ab initio* DZ vertical transition energies to 5π states are probably too small by about the same.

(40) T. H. Dunning, Jr., private communication.

(41) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 3, Van Nostrand, Princeton, N. J., 1967.

(42) (a) C. F. Bender and E. R. Davidson, *J. Phys. Chem.*, **70**, 2675 (1966); (b) C. F. Bender and E. R. Davidson, *J. Chem. Phys.*, **47**, 360 (1967); (c) H. F. Schaefer III and C. F. Bender, *ibid.*, **55**, 1720 (1971).

Table II. Optimum Geometries for Ozone

		$^1A_1(4\pi)$			$^3B_2(4\pi)$		
			Ab initio			*Ab initio*	
		INDO–MBS	MBS	DZ	INDO–MBS	MBS	DZ
GVB(1)	*R*, Å	1.19	1.35	1.38	1.21	1.38	1.45
	θ, deg	118	113		111	110	
Exptl	*R*, Å		1.278				
	θ, deg		116.8				

splitting of the $1a_2(\pi)$ orbital of the HF wave function with the $2b_1(\pi)$ orbital. Similarly, the $^1A_1(6\pi)$ state involves splitting of the $4a_1$(n or σ) orbital with the $3b_2$(n or σ) orbital. (*N.b.*, the orbitals arising from 1s basis functions were not included in numbering the orbitals.) The INDO–HF open-shell states were calculated using the open-shell methods of Hunt, Goddard, and Dunning,[43,44] designed to ensure full convergence.

II. Results

A. Vertical Excitation Energies. The vertical excitation energies for ozone (using the experimental geometry) are shown in Table I. We see that for both the GVB(1) and the CI calculations the *ab initio* MBS results are in good agreement with the *ab initio* DZ results for the first eight states. The INDO calculations give somewhat poorer results. Comparing the INDO and *ab initio* MBS–GVB(1) results, the $^1A_1(4\pi) \rightarrow {}^3B_2(4\pi)$ excitation energy is reproduced exactly, while INDO appears to underestimate each n → π excitation by ~0.2 eV or 10%. However, the fairly good agreement may be fortuitous, since the use of the optimum theoretical geometries rather than the experimental geometries leads to INDO transition energies (vertical; 1.17 eV; adiabatic; 1.05 eV) much larger than the *ab initio* (vertical; 0.24 eV; adiabatic, 0.22 eV).

Comparing INDO and *ab initio* MBS–CI results, we see that the agreement is not as good as for GVB(1) calculations. For INDO the $^3B_2(4\pi) - {}^1A_1(4\pi)$ separation is low by 0.22 eV or 20%, the four 5π states are all high by about 0.6 eV or 30%, and the 6π states are too high by 0.73 and 0.83 eV or about 20%. The $^1B_2(4\pi)$ state in INDO is also high by 1.18 eV or about 15%, but this ionic state is not well described by the MBS *ab initio* wave function either.

B. Geometries. The calculated geometries for the $^1A_1(4\pi)$ and $^3B_2(4\pi)$ states using GVB(1) are listed in Table II. The bond *angles* from INDO and *ab initio* MBS calculations are in good agreement with each other and experiment (for $^1A_1(4\pi)$). The bond *lengths*, on the other hand, differ greatly, INDO giving bond lengths that are too short by 0.17 Å. In passing, we note that it is important to use equivalent bases and wave functions for these comparisons, since systematic errors in bond lengths are expected.[45,46] The short OO bonds obtained with INDO for ozone are to be expected since for open-shell HF calculations on ground state $O_2(^3\Sigma_g^-)$, INDO gives $R = 1.140$ Å,[31] while *ab initio* MBS calculations give $R = 1.217$ Å[46] (experimental $R = 1.207$ Å[31]). Moreover, INDO calculations using a closed-shell HF wave function yielded a ground state bond length for ozone too short by 0.11 Å[46] and for H_2O_2 an OO bond length too short by 0.255 Å.[31,47]

Despite the good agreement on bond angles described above for INDO and *ab initio* MBS calculations, decreasing the bond angle below 90° leads to disastrous results with INDO. The four 5π and two 6π states all drop significantly in energy as the bond angle decreases, whereas all but one of these states should *increase* in energy. Moreover, the energy of the $^1A_1(6\pi)$ ring state (60°) is *6.74 eV below* the energy of the open $^1A_1(4\pi)$ state (the real ground state)! In the *ab initio* MBS description[9a] this ring state is nearly degenerate with the $^1A_1(4\pi)$ state. Hence, INDO gives a ring energy too low by about 6.7 eV.

For the four 5π and the $^3B_2(6\pi)$ states, *ab initio* MBS calculations lead to strictly repulsive potential curves as the bond angle is decreased below 90°. INDO calculations on these states, however, lead to potential curves with a double minimum, the correct one at large angles (100–130°) and a spurious one at small angles (60°). However, the error in the INDO description of the 5π states is less than that for the 6π states. INDO–GVB(1) calculations lead to a vertical excitation energy (at 60°) from the $^1A_1(6\pi)$ to the 5π states of about 6.5 eV, which is only ~2.5 eV greater than the comparable *ab initio* MBS value (~4 eV[48]). Thus, the INDO energies of the 5π states are about 3 to 4 eV too low for small angles.[49] As a result, while *ab*

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(43) W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., *Chem. Phys. Lett.*, **6**, 147 (1970).

(44) The CNINDO program[31] from QCPE handles open-shell states *via* the unrestricted HF(UHF) method. The program can only calculate one state for each spin. More importantly, one cannot be sure that the state obtained is the lowest in energy for that spin, since the trial guess is taken from an EHT calculation and may lead to the wrong state. For example, in ozone the CNINDO program leads to the $^3A_2(5\pi)$ state instead of the $^3B_2(4\pi)$ state. Moreover, the energy of the $^3A_2(5\pi)$ state calculated by CNINDO is not reliable for two reasons. First, the CNINDO program assumes that the HF orbitals will have C_{2v} symmetry. In fact, the optimum orbitals are asymmetric; forcing them to be symmetric, as in the CNINDO program, increases the energy by 2.75.[34] Second, this program uses the unrestricted Hartree–Fock (UHF) wave function, which is a Slater determinant (just as in HF) but with up spin orbitals allowed to be different than down spin orbitals. Generally, the UHF wave function leads to similar energies as HF, but for the $^3A_2$ state of ozone we find the UHF energy to be 0.63 eV lower (for orbitals of C_{2v} symmetry). The use of UHF for open shell states and HF for closed shell states can lead to inconsistent descriptions with respect to correlation energy. Using general open-shell techniques,[43] we avoided these problems.

(45) *Ab initio* MBS wave functions generally overestimate bond lengths, since a MBS does not have enough flexibility to describe the contraction of the wave function that occurs upon bond formation. On the other hand, *ab initio* HF wave functions generally underestimate bond lengths, because the wave function dissociates improperly. Consequently, the use of HF with MBS leads to a cancellation of errors and, as a result, often gives good bond lengths. (See, for example, the extensive studies by Pople[46] and coworkers.)

(46) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

(47) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).

(48) P. J. Hay, private communication. The 5π states ($^{1,3}A_2$, $^{1,3}B_1$) at 60° may be viewed as excited states relative to the $^1A_1(6\pi)$ state, arising from a $\pi \rightarrow \sigma^*$ promotion.

(49) Although *ab initio* results on the 4π states are not available at 60° for comparison, the absence of a double minimum in the INDO potential curves indicates (along the results on the 5π states) that the preference for small angles in the INDO description of the states of ozone is proportional to the number of π electrons.

initio calculations lead to 5π states at 60° with energies about 3 eV *above* the comparable states at 117°, the INDO calculations lead to 5π states at 60° with energies about 0 to 1 eV *below* the comparable states at 117°.

III. Discussion

The most grievious fault of INDO apparent in our calculations on ozone is the strong bias toward closed geometries,[50] even when unfavorable electron interactions should make small bond angles strictly repulsive, *e.g.*, for the $^1A_1(5\pi)$, $^3A_2(5\pi)$, $^1B_1(5\pi)$, $^3B_1(5\pi)$, and $^3B_2(6\pi)$ states. Similar problems with INDO have been found previously.[51] It appears as if INDO does not properly represent the repulsion involved when triplet-coupled electrons are forced into close proximity. In addition it appears that INDO gives rise to π bonds that are far too strong. The latter explanation would be consistent with the short bond lengths observed for $^1A_1(4\pi)$ and the large transition energies observed for the $4\pi \rightarrow 5\pi$ and $4\pi \rightarrow 6\pi$ transitions (at the calculated equilibrium geometry). Consequently, the use of INDO for calculating equilibrium geometries as in conformational studies or reaction pathways is very risky, even if correlation effects are included.

Our calculations show that INDO treats the electron correlations involved in the GVB(1) wave function fairly well, so that using such correlated wave functions will cure some of the gross errors encountered when INDO is used with the HF method. However, introduction of CI need not improve the energy spectrum obtained with INDO and, in fact, may make it worse. (See, for example, the reordering of the 5π and 6π states after CI.) Nevertheless, despite certain significant errors in describing the overall energy spectrum, INDO does reproduce many of the energy separations properly, *e.g.*, the singlet–triplet splittings of states arising from the same configurations. This indicates to us that it may be possible to develop a method on the order of INDO in complexity that would yield reliable results (comparable at least to *ab initio* MBS calculations). Work is in progress along these lines.

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(50) Subsequent to submission of this paper, A. K. Q. Siu and E. F. Hayes, *Chem. Phys. Lett.*, **21**, 573 (1973), published semiempirical HF calculations on the open (1^1A_1) and ring (2^1A_1) states of ozone, in which they reported that the CNDO/2, INDO, and MINDO approximations all favored the ring state by 5 to 10 eV over the open state, in agreement with our results. Siu and Hayes also reported *ab initio* Hartree–Fock calculations, leading to the ring state about 0.36 eV above the open ground state. However, as shown earlier from *ab initio* GVB and CI calculations, HF wave functions (which exclude electron correlations) are biased in favor of the ring state by 1 eV or more, so that the *ab initio* relative energy (0.39 eV) of the ring and open states obtained by Siu and Hayes is much smaller than the real spacing between these states. Extensive DZ–CI calculations[9c] indicate that the ring state is 1.57 eV above the open ground state.

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Symmetry Adapted Functions and Normalized Spherical Harmonic (NSH) Hamiltonians for the Point Groups O_h, T_d, D_{4h}, D_{2d}, C_{4v}, D_{2h}, C_{2v}

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Abstract: A general method is introduced for the projection of normalized spherical harmonic (NSH) Hamiltonians. Subgroups of O_h which subduce C_{2v} are specifically considered, and d^n basis functions symmetry adapted to the various groups are derived. The advantages of a symmetry-adapted basis are emphasized in the interpretation of absorption spectra of three nickel(II) systems characterized by C_{2v} effective symmetry. Symmetry-adapted representations of H_G for $G = O_h$, T_d, D_{4h}, C_{4v}, D_{2d}, D_{2h}, and C_{2v} are tabulated for the d^1 (and d^9) configuration, the spin triplet states of the d^2 (and d^8) configuration, and the spin quartet states of the d^3 (and d^7) configuration.

Although the absorption spectra of many transition metal systems have been reproduced using a ligand field Hamiltonian and l^n basis set,[1-3] calculations assuming D_{2d}, D_{2h}, or C_{2v} symmetry are not common.[4-7] Hamiltonians for D_{2h} or C_{2v} symmetry and a d^n basis set incorporate a maximum of five empirical parameters (excluding interelectronic repulsion parameters), in contrast to a maximum of three such parameters for symmetries with a fourfold axis. Spectra are therefore often interpreted assuming the symmetry of a higher point group for calculation purposes. Only in certain cases can the assumption be justified.[8] We present a method for the projection of normalized spherical harmonic (NSH) Hamiltonians which is applicable to all point group symmetries and offers not only the possibility of straightforward calculations for noncubic as well as cubic symmetries but also the possibility of

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