The $\tilde{X}\,^1A_1 \rightarrow \tilde{A}\,^1B_1$ transition moment of H_2O using state-specific configuration-interaction wave functions

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We report the results on the oscillator strength of the H_2O $\tilde{X}\,^1A_1 \rightarrow \tilde{A}\,^1B_1$ transition from two types of calculations. One from using correlated state-specific wave functions for each state and one from using large MRD-CI wave functions with a common basis set. In the first case nonorthonormality is considered explicitly via the use of corresponding orbitals. Both types of calculation converge to a value of $f = 0.065$. This result agrees with one experimental value ($f = 0.060$) and disagrees with the most recent theoretical calculation which employed the Stiltjes imaging method ($f = 0.021$). As is the case with previous atomic calculations, the state-specific approach improves the quality of the wave functions of excited states while reducing their size considerably.

I. INTRODUCTION

The spectrum and properties of excited states of H_2O have been attracting attention for many years. The lowest lying, and most intense in the absorption, $\tilde{A}\,^1B_1$ state has been assigned experimental oscillator strengths ranging from $f = 0.046$ to 0.060.[1,2] The first experiment involves photon absorption while the second involves inelastic electron scattering.

A larger dispersion exists among the published theoretical results,[3–9] in spite of the fact that they have taken into account electron correlation to some degree of approximation. For example, single excitations configuration-interaction (CI) calculations by Wood[3] and Dierksen *et al.*[9] have yielded $f_L = 0.037$ and 0.021, respectively, in the length formulation.[10] A low order equations of motion (EOM) calculation by Yeager *et al.*[4] yielded $f_L = 0.050$ while the equivalent time-dependent Hartree–Fock (TDHF) calculation of Williams and Langhoff[7] yielded $f_L = 0.036$. The CI calculations of Buenker and Peyerimhoff,[5] carried out in their multireference double excitations (MRD) scheme, gave $f_L = 0.059$ and $f_V = 0.078$. The corresponding energy independent geometric mean is $\sqrt{f_L f_V} = 0.068$. And finally, two many-electron calculations which are based on the concept of preselecting those correlation vectors which contribute the most to transition moments[6,8] yielded $\sqrt{f_L f_V} = 0.046$ (Ref. 6) and $\sqrt{f_L f_V} = 0.067$ (Ref. 8). These last two computations follow from the general arguments and analysis of the photoabsorption process put forth earlier by Nicolaides and Beck.[11–14]

We point out that the observed discrepancies occur for the strongest feature of the discrete spectrum, for which the expected reliability of the calculations—as compared with that of the weaker peaks—is higher and, in principle, less sensitive to choices of basis sets.

Especially interesting is the large difference (a factor of 3) between the recent Stiltjes imaging prediction[9] and our previous CI calculations.[5,8] In fact, it is this difference which prompted us to reexamine this transition. Methods employing the Stiltjes imaging construct the discrete as well as part of the continuous intensity spectrum at the single excitations CI level. Thus, it is appropriate to understand their degree of reliability and usefulness.

The details of the dynamics of excitation involve three major components: electron correlation in the ground state, relaxation, and electron correlation in the excited state. In most cases, it is the last two components which are difficult to incorporate accurately with methods which employ a single basis set. This is accentuated in situations of valence-Rydberg mixing (e.g., see articles by Buenker and Peyerimhoff, Beck and Nicolaides, and von Niessen, Domcke, and Cederbaum in Ref. 15), whether this occurs in the discrete or the continuous spectrum (e.g., Refs. 13 and 16).

In most cases, in order to ensure reasonable accuracy of a calculation of transition probabilities in many-electron atoms or molecules, advanced theoretical and computational approaches must be applied.

In this paper we present the results of many-electron calculations on this f value which were carried out by using *state-specific* N-electron function spaces, optimized separately for initial and final states. A state-specific theory for atomic and molecular properties yields compact but accurate wave functions from variational calculations based on a multiconfigurational Fermi–Sea zeroth order vector.[13,17–22] An intrinsic computational difficulty in such an approach is the *nonorthonormality* (NON) contributions to off-diagonal matrix elements. The present results are obtained by taking NON between CI functions fully into account, by implementing the theory of corresponding orbitals as presented by King *et al.*[13,23]

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For purposes of comparison we have also produced new MRD-CI results which use a common basis set for ground and excited states.[24] Both results are in agreement with our earlier work[5,8] and with experiment and differ from the recent single-excitation CI-Stiltjes imaging-results of Dierksen *et al.*[9]

II. STATE-SPECIFIC WAVE FUNCTIONS AND THE INCLUSION OF NONORTHONORMALITY (NON) IN TRANSITION PROBABILITY CALCULATIONS

Separate choice and optimization of the N-electron function spaces describing different states or different parts of the wave function of the same state results, in general, in basis sets which are not orthonormal between them. The conceptual and computational advantages of this *state-specific* approach have been reviewed.[20,21]

For wave functions expanded in terms of atomic orbital or molecular orbital determinants, NON can be taken into account by explicit computation of the cofactors or by the method of corresponding orbitals proposed by King *et al.*[23] This method was first applied to the calculation of transition probabilities by Westhaus and Sinanoglu[25] for electric dipole and by Nicolaides *et al.*[26] for quadrupole radiation, taking advantage of the symmetry of the transition operator.

The subsequent work of Nicolaides and Beck[12,13] showed that the magnitude of the NON calculations can be reduced significantly if symmetry adapted configurations instead of determinants are processed. It was also shown that for ionized systems the effects of NON are negligible, while for neutral (or even singly ionized) systems, when they are treated in a state-specific manner, NON effects are often enhanced decisively, especially among the major configurations and correlation vectors. Explicit calculation of NON then allows for new and systematic interpretations of phenomena such as photoabsorption to multiply excited states,[13,27] charge transfer due to symmetry breaking,[22] or autoionization processes.[28,29]

The approach of the present work is yet another application of the corresponding orbitals method[23] suitable for large polyatomic molecular calculations.[30] It is formulated and implemented in a most general way in terms of density matrices and has been applied to molecular calculations of small Hamiltonian matrices,[22] as well as to transition probabilities. Its main elements are as follows:

Given a set of molecular orbitals $\{a\}$ and $\{b\}$ which are not orthonormal between them, according to King *et al.*[23] two unitary transformations can produce new sets $\{\hat{a}\}$ and $\{\hat{b}\}$, which are orthonormal between them. In terms of the atomic orbital basis sets $\{x\}$ we then have

$$\hat{a}_i = \sum_p^m \sum_k^n f_{pK} V_{Ki} x_p = \sum_{p=1}^m d'_{pi} x_p \tag{1}$$

and

$$\hat{b}_i = \sum_q^m \sum_l^n c_{ql} U_{li} x_q = \sum_{q=1}^m c'_{qi} x_q, \tag{2}$$

where **f** and **c** are the original expansion coefficients and **V** and **U** are the unitary matrices diagonalizing the original overlap matrix **D** between $\{a\}$ and $\{b\}$.

The dipole transition integral over determinants Δ_A and Δ_B becomes

$$T_d = \langle \Delta_B | d | \Delta_A \rangle$$

$$= \det(\mathbf{U}) \det(\mathbf{V}^+) \prod_{j=1}^n d_j \sum_q^m \sum_p^m \mathrm{Den}(q, p) \langle x_q | d | x_p \rangle \tag{3}$$

if all $d_j > 0$ (where d_j are the eigenvalues of the overlap matrix **D**) or

$$T_d = \det(\mathbf{U}) \det(\mathbf{V}^+) \prod_{j \neq K}^n d_j \sum_q^m \sum_p^m E_K(q, p) \langle x_q | d | x_p \rangle \tag{4}$$

if

$$d_j > 0, \quad \forall \quad j \neq K, \quad d_K = 0$$

with

$$\mathrm{Den}(q, p) \equiv \sum_{i=1}^n c'_{qi} d'_{pi} / d_i \tag{5}$$

and

$$E_K(q, p) \equiv c'_{q_K} d'_{p_K}. \tag{6}$$

T_d is zero if the overlap matrix has more than one singularity, i.e., more than one d_i is zero.

III. CALCULATION OF THE WAVE FUNCTIONS

The calculations were carried out for the vertical transition, at the experimental geometry of the ground state minimum, with O–H of 1.809 bohr and HOH angle of 104.52°.

Two types of wave functions were produced, reflecting two different approaches to the calculation of excited states at the correlation level. In the first case, a common MO basis set is used for the ground and excited states. In the second, two different MO basis sets are employed and optimized separately for each state. In these calculations, the same atomic basis (AO) set was used—although this is an approximation to the fully optimum theory.[20,21] [An example of a well converged molecular calculation (electron correlation in CH_4) with suitably optimized basis sets can be found in the recent work of Beck and Kunz[31]].

The AO basis set was, as before,[8] double zeta GTO, 9*s*5*p*/5*s*3*p* for oxygen and 4*s*/3*s* for H.[32] Added to these were polarization functions [*d*-type (0.88) for oxygen and *p*-type (1.0) for hydrogen] and diffuse functions on oxygen [*s*-type (0.032) and *p*-type (0.028)]. Such a basis set has been found adequate for the description of the first few Rydberg states of H_2O, at vertical energies lower than about 10 eV.[5] Our conjecture is that further addition of Rydberg functions would not alter our results significantly.

In the state-specific calculations, we first obtained the SCF MOs for each state [$\tilde{X}\,^1A_1$ and $\tilde{A}\,^1B_1(1b_1 4a_1(3s))$]. Then, a number of MRD-CI wave functions[24] were generated at the four main configurations 1 root level (4M/1R). The size of these wave functions was determined

TABLE I. The sets of reference configurations[a] used in the MRD-CI calculations.

Treatment	$\tilde{X}\,^1A_1$	$\tilde{A}\,^1B_1$
4M/1R	$2a_1^2 3a_1^2 1b_2^2 1b_1^2$	$2a_1^2 3a_1^2 1b_2^2 1b_1 4a_1$
	$2a_1^2 3a_1^2 1b_2^2 1b_1 2b_1$	$2a_1^2 3a_1^2 1b_2^2 1b_1 5a_1$
	$2a_1^2 1b_2^2 1b_1^2 3a_1 4a_1$	$2a_1^2 1b_2^2 1b_1^2 3a_1 2b_1$
	$2a_1^2 3a_1^2 1b_1^2 1b_2 2b_2$	$2a_1^2 1b_2^2 1b_1^2 3a_1 3b_1$
	In addition to the four above,	In addition to the *first two* above,
10M/1R	$3a^2 1b_2^2 1b_1^2 2a_1 4a_1$	$2a_1^2 3a_1^2 1b_2^2 1b_1 6a_1$
	$2a_1^2 1b_2^2 1b_1^2 3a_1 6a_1$	$2a_1^2 3a_1^2 1b_2^2 4a_1 2b_1$
	$2a_1^2 1b_2^2 1b_1^2 3a_1 8a_1$	$2a_1^2 3a_1^2 1b_2^2 4a_1 3b_1$
	$2a_1^2 3a_1^2 1b_2^2 1b_1 3b_1$	$3a_1^2 1b_2^2 2a_1 4a_1 6a_1 1b_1$
	$2a_1^2 3a_1^2 1b_1^2 1b_2 3b_2$	$2a_1^2 1b_2^2 3a_1 4a_1 6a_1 1b_1$
	$2a_1^2 3a_1^2 1b_1^2 1b_2 5b_2$	$2a_1^2 1b_2^2 3a_1 4a_1 8a_1 1b_1$
		$2a_1^2 3a_1^2 4a_1 1b_1 1b_2 3b_2$
		$2a_1^2 3a_1^2 4a_1 1b_1 1b_2 5b_2$

[a] In all cases we have the oxygen core orbital doubly occupied ($1a_1^2$).

by choosing different threshold values[24] ranging from 0.7 $\times 10^{-3}$ to 0.1 $\times 10^{-3}$ a.u. The application of these wave functions to the calculation of the corresponding f value (including nonorthonormality) gave us a convergence trend (see the next section).

Apart from the above calculations, large, common basis MRD-CI wave functions were obtained and corresponding f values with 4M/1R and 10M/1R, $T = 1$ μH. The reference configurations are listed in Table I. In all cases, the oxygen $1s$ orbital was kept doubly occupied while its complement in the virtual space was not included in the CI.

IV. RESULTS AND CONCLUSIONS

Our results are presented in Tables II and III. Since the emphasis is on the characteristics of the wave functions, the experimental energy difference ($E = 0.2734$ a.u.) is used throughout. In Table II we list four sets of f_L and f_V obtained with different SCF functions. It is seen that for ground state MOs the f_L and f_V are the smallest and closest to those obtained using the $1b_1$ SCF orbital of the ground state and the $4a_1$ SCF orbital of the excited state[33]

TABLE II. Comparison of different SCF values for the length (f_L) and velocity (f_V) oscillator strengths of $\tilde{X}\,^1A_1 \rightarrow \tilde{A}\,^1B_1$ transition. The experimental energy is used so that analysis is confined to the transition matrix element.

	f_L	f_V
a	0.034	0.047
b	0.015	0.073
c	0.036	0.054
d	0.045	0.095

[a] Using the orbitals $1b_1$ and $4a_1$ obtained from a single SCF calculation on the ground state. This work.
[b] Using the orbitals $1b_1$ and $4a_1$ obtained from a single SCF calculation on the excited state. This work.
[c] Using the $1b_1$ and $4a_1$ orbitals of each SCF wave function but without incorporation of nonorthonormality. Reference 33.
[d] Using the N molecular orbitals of each state obtained self-consistently. Nonorthonormality is included. This work.

without nonorthonormality (NON). The excited state MOs decrease f_L and increase f_V. Finally, an increase in both f_L and f_V is observed when NON is accounted for explicitly. These N-electron SCF f values differ between them by a factor of 2 ($f_L = 0.045$, $f_V = 0.095$), but they are close to our previous results obtained with the MRD-CI[5] ($f_L = 0.059$, $f_V = 0.078$) or the first-order theory of oscillator strengths FOTOS[8] ($f_L = 0.044$, $f_V = 0.100$) many-electron approaches.

Table III shows the results of our two types of calculation. The state-specific NON results, for different threshold values, indicate a very slow convergence towards higher values for f_L and towards lower values for f_V. Their final, geometric average value is $\sqrt{f_L f_V} = 0.065$. This value agrees with our previous[5,8] results of $\sqrt{f_L f_V} = 0.068$ and 0.067, respectively, as well as with our present more extensive MRD-CI results (see Table III) of $\sqrt{f_L f_V} = 0.065$ (with ground state MOs) and $\sqrt{f_L f_V} = 0.070$ (with excited state MOs). This evidence suggests that the oscillator strength for this transition is around $f = 0.065$.

This value agrees with the experimental one of Ref. 2 ($f = 0.060$) but disagrees with the theoretical value of Ref. 9 ($f = 0.02$), where the Stiltjes imaging approach was applied. This difference may be due to orbital relaxation and the slight valence-Rydberg mixing in the $\tilde{A}\,^1B_1$ state.[34] It appears that the single excitations CI with a single basis set does not account for this accurately and the Stiltjes imaging cannot correct for this by redistributing oscillator strength towards the low lying states. We note that the state-specific theory has been compared before with the Stiltjes imaging approach in the case of an atomic photoexcitation spectrum, that of boron, where valence-Rydberg mixing occurs. The results of Beck and Nicolaides[35] differ from those of Nesbet[36] not only quantitatively for each individual transition but also qualitatively, in terms of the overall distribution of oscillator strength. These early results agree with recent observations (e.g., Ref. 37) of deviations of the standard static-exchange, separated-channel approximation to Stiltjes imaging from experimental cross sections in regions where autoionizing states are present.

TABLE III. Oscillator strengths from the present calculations. One set of calculations—under the heading state specific—involves a series of calculations using MRD-CI wave functions for each state for different threshold values (and, correspondingly, different size of the CI expansion). For the calculation of the f values, nonorthonormality is accounted for explicitly. The other set of calculations involves two large MRD-CI calculations, one with ground state MOs, and the other with excited state MOS. Experimental wavelengths are used throughout. For the large MRD-CI calculations, the values obtained from using the theoretical wavelengths are also given in parentheses. For the largest state-specific calculation (last line), the energy difference ΔE is 0.268 a.u. For the MRD-CI with ground state MOs, ΔE = 0.269 a.u. and for MRD-CI with excited state (MOs, ΔE = 0.275 a.u. the experimental ΔE is 0.273 a.u.

$\tilde{X}\ ^1A_1$		$\tilde{A}\ ^1B_1$			
T (threshold) $\times 10^3$ a.u.	Number of symmetry adapted functions (SAFs)	T $\times 10^3$ a.u.	SAFs	f_L	f_V
		State specific			
	SCF		SCF	0.045	0.095
	SCF	0.1	485	0.043	0.086
0.1	507		SCF	0.048	0.086
0.7	76	0.7	40	0.044	0.095
0.6	95	0.4	91	0.043	0.096
0.4	150	0.4	91	0.045	0.095
0.3	211	0.2	212	0.046	0.092
0.2	284	0.2	212	0.048	0.088
0.1	507	0.1	485	0.049	0.085
		MRD-CI			
Ground state MOs					
0.001	1741	0.001	6508	0.052(0.051)	0.082(0.084)
Excited state MOs					
0.001	5598	0.001	3483	0.056(0.057)	0.085(0.085)
Experimental			0.046 (Ref. 1)		0.060 (Ref. 2)

Finally, it should be noted that, when using the orthonormal basis sets, optimized for one of the states, it was found necessary to increase the set of reference configurations for the other state in order to have a balanced treatment in terms of $\sum c_0^2$ of the reference configurations in the final wave function, while keeping T at 1.0 μH. As a result, relatively large expansions were obtained for the states when using nonoptimum basis sets. In this way, it was possible to account for NON in this system, within the MRD-CI method, as shown by the close agreement found in f values obtained with the MRD-CI method. However, for other systems it may not be possible to deal with NON in this manner (see, e.g., Ref. 30) and the use of a method such as the one presented here is necessary.

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