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Calculation of molecular mean excitation energies via the polarization propagator formalism: H_2 and H_2O

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We present *ab initio* calculations of oscillator-strength sum rules $S(\mu)$ and mean exciton energies I_μ for $-1 \leq \mu \leq 1$. We use the polarization propagator formalism at the random-phase approximation level. Calculations are performed for H_2 and H_2O using large basis sets: 90 uncontracted Gaussian-type orbitals (CGTO's) for H_2 and 101 CGTO's for water. We find that $I_0 = 19.12$ eV for H_2 (including thermal averaging) and 72.46 eV for H_2O. They agree very well with previous semiempirical estimates. The same holds for the other I_μ moments. The fulfillment of the Thomas-Reiche-Kuhn sum rule in both the dipole length and velocity formulations shows that the basis sets employed are satisfactory. We have also investigated the "shell-wise" contributions to $S(0)$ and I_0 for H_2O.

I. INTRODUCTION

The characteristic quantities which describe the interaction of radiation with matter are the moments of the target oscillator strength distribution

$$S(\mu) = \sum\!\!\!\!\!\!\!\int E^{\mu} \frac{df}{dE} dE \; , \tag{1}$$

$$L(\mu) = \sum\!\!\!\!\!\!\!\int E^{\mu} \ln E \frac{df}{dE} dE \; , \tag{2}$$

and the associated mean excitation energies

$$I_\mu = 2R \exp[L(\mu)/S(\mu)] \; , \tag{3}$$

where R is the Rydberg energy and the summation is over all transitions, including the entire continuum. Of particular interest to us has been the study of energy deposition by swift, massive particles impinging on material foils. The stopping and straggling are related to the $\mu = 0, 1$ moments mentioned above[1,2] through a logarithm[1] of the appropriate mean excitation energy.[3] Other properties are also related to oscillator strength distribution moments such as the Lamb shift ($\mu = 2$), electronic excitation ($\mu = -1$), and the static polarizability ($\mu = -2$).

Determination of I_0 has traditionally been experimental, as a theoretical determination is difficult, requiring a knowledge of the complete oscillator strength distribution for the target, including the continuum. Bethe[1] calculated I_0 for the hydrogen atom from the exact wave function, and Inokuti and co-workers[4] have calculated orbital and whole-atom values of oscillator strength moments directly from Hartree-Fock-Slater atomic wave functions.

Another approach, based on ideas from the uniform electron gas, was taken by Lindhard and Scharff.[5] As the plasma frequency of a uniform electron gas depends only on the electron density, they suggested that an atom be treated as a free, inhomogeneous electron gas, with a local plasma frequency $\omega_p(\mathbf{r})$ which depends on the local electron density $\rho(\mathbf{r})$ as

$$\omega_p(\mathbf{r}) = [4\pi e^2 \rho(\mathbf{r})/m_e]^{1/2} \; . \tag{4}$$

This model, called the local plasma approximation (LPA), then derives an expression for I_0 using dielectric response theory

$$Z \ln I_0 = \int \rho(\mathbf{r}) \ln[\gamma h \omega_p(\mathbf{r})] d^3\mathbf{r} \; . \tag{5}$$

The (empirical) parameter γ was originally introduced by Lindard and Scharff in order to help to account for single-particle excitations in atoms. They used $\gamma = \sqrt{2}$, as did Chu and Powers[6] later when calculating atomic I_0's. More recently it has been suggested[7] that other values of γ might be used.

Other methods for obtaining I_0 such as that of moment theory[8] or the method of Chan and Dalgarno[9] have also been utilized.

Several semiempirical methods[10] for calculating atomic mean excitation energies have also been employed, such as that of Dalgarno[11] or the dipole oscillator strength distribution (DOSD) scheme of Zeiss and Meath.[12,13] Both of these methods use experimental information to construct an oscillator strength distribution from which moments can be extracted.

When one moves to molecular targets, things become more difficult, as the information required for any of the methods mentioned above becomes more complicated and difficult to obtain. Until recently,[13] the only theoretical molecular results were those obtained for H_2 from very accurate *ab initio* molecular wave functions,[14] from moment theory,[8] or from the semiempirical DOSD results of Meath *et al.* on a variety of molecules.[12,15–23] In the past year or so, however, several papers have appeared which report calculations of molecular mean excitation energies based on the LPA (Refs. 7 and 24–32) [Eq. (4)], and there has been one paper where the oscillator strength moments, $S(\mu)$ and $L(\mu)$ ($-6 \leq \mu \leq 2$), of N_2 have been evaluated directly from a local-density-functional wave function.[33]

Although determination of molecular mean excitation energies via the semiempirical DOSD scheme produces excellent results, it relies on extensive experimental input, and thus is not useful for an arbitrary molecule if the experimental measurements have not been made. The LPA method does not suffer from this drawback, but has several other problems. The biggest problem seems to be that the LPA formula for I_0 [Eq. (5)] cannot be obtained from the definition of I_0 in terms of oscillator strength moments.[34] In addition, the usual implementation[27–32] of LPA utilizes the Gordon-Kim[35] density rather than more realistic densities for the molecules. There should be no problem, however, in using the same formalism in conjunction with more accurate molecular densities. More serious problems stem from the lack of an unambiguous choice of γ [Eq. (5)] and the lack of an obvious way to obtain I_μ for $\mu \neq 0$.

Kosman and Wallace's explicit calculation of the oscillator strength distribution of N_2 (Ref. 33) is based on the multiple-scattering formalism[36] in conjunction with the local exchange ($X\alpha$) approximation.[37] This scheme generates a complete oscillator strength distribution and does the explicit integrals of Eqs. (1) and (2) to obtain oscillator strength moments. There is a problem, however, in that the method is grounded in density-functional theory, which is developed for the ground-state density. The procedure forms approximations to excited states as antisymmetrized products of the problem's eigenvectors,[36] although it is not clear that the identification of these eigenvectors with one-electron spin orbitals is justified.[38] An additional ambiguity is encountered in the choice of the Slater exchange parameter α.

It seems clear, then, that it would be useful to have a series of molecular calculations of oscillator strength moments and related properties which can be used for comparison, and which are obtained from a well-defined *ab initio* theory which is based on first principles and which has been tested in calculations of similar properties. The random-phase approximation (RPA) was chosen to serve that purpose since it is well established that singlet excitation spectra come out well in that method. We thus present below several properties of the oscillator strength distributions of H_2 and H_2O calculated with the first-order polarization propagator formalism (which is identical to the random-phase approximation). This is the first such *ab initio* calculation of the oscillator strength distribution of water.

II. METHOD

The calculations reported below were carried out using the MUNICH program system.[39] Using a variety of basis sets (*vide infra*), the excitation energies and oscillator strengths were calculated using the polarization propagator formalism. As the method is well documented in both its formal[40] and computational[41] aspects, it will not be described in detail here. Suffice it to say that this is a method for direct calculation of excitation energies and oscillator strengths. We compute the differences directly from the propagator without knowing the wave functions and energies of the individual states.

The initial step in a propagator calculation generally consists of performing a self-consistent-field (SCF) calculation on the reference state, which in the present applications is the ground state. The SCF orbitals and orbital energies are then used to compute the polarization propagator, the poles and residues of which are the excitation energies and transition moments, respectively. The polarization propagator is evaluated in a perturbative way using the fluctuation potential (electron-electron interaction minus the Fock potential) as the perturbation. Through first order in the fluctuation potential we arrive at a well-known approximation, the RPA, which may also be derived in many other ways. Using configuration-interaction (CI) language, the RPA excitation energies roughly correspond to those obtained for singles and doubles CI.

Moments of the oscillator strength distribution are obtained by direct evaluation of Eqs. (1)–(3). Since we are using a finite Gaussian basis set, the continuum is represented by a set of discrete states above the ionization limit so the sums in Eqs. (1) and (2) may be done explicitly. As the Thomas-Reiche-Kuhn (TRK) sum rule[42] is *not*

TABLE I. Basis sets and SCF energies for H_2 calculations ($R = 1.4011$ a.u.).

Basis number	Primitive basis	Contrasted basis	Number of CGTO's	E_{SCF} (a.u.)
4[a]	(2*s*)	[2*s*]	4	−1.093 426
12[b]	(6*s*, 1*p*)	[3*s*, 1*p*]	12	−1.131 643
24[c]	(10*s*, 2*p*)	[6*s*, 2*p*]	24	−1.133 497
60[d]	(10*s*, 5*p*, 2*d*)	[6*s*, 4*p*, 2*d*]	60	−1.133 604
78[e]	(13*s*, 7*p*, 2*d*)	[9*s*, 6*p*, 2*d*]	78	−1.133 606
90[f]	(13*s*, 7*p*, 3*d*)	[9*s*, 6*p*, 3*d*]	90	−1.133 608

[a] From Huzinaga (Ref. 45), (2*s*) basis.

[b] Huzinaga (Ref. 45) (6*s*) basis augmented with one *p* function ($\zeta_p = 0.75$).

[c] van Duijneveldt (Ref. 46) (10*s*) basis augmented with two *p* functions ($\zeta_p = 1.5, 0.3$).

[d] van Duijneveldt (Ref. 46) (10*s*) basis augmented with *p* and *d* functions from Schulman and Kaufman (Ref. 47) and an additional *d* function ($\zeta_d = 5.00$).

[e] Basis 60 augmented with three diffuse *s* ($\zeta_s = 0.024\,863, 0.009\,945, 0.003\,978$) and two diffuse *p* ($\zeta_p = 0.08, 0.032$) functions.

[f] Basis 78 augmented with one *d* function ($\zeta_d = 0.8$).

TABLE II. H_2 oscillator sum rules calculated in the random-phase approximation [$S(1)$ in a.u., I_μ in eV], in dipole length (L) and dipole velocity (V) formulations.

	Basis sets						Accepted value
	4	12	24	60	78	90	
$S^L(0)$	0.714	2.382	2.086	2.027	2.000	2.000	2.000[a]
$S^V(0)$	0.593	1.321	1.886	1.973	1.997	1.998	
I_0^L	16.180	32.109	20.274	19.724	19.463	19.445	19.2[b]
I_0^V	16.050	26.351	20.995	19.815	19.439	19.443	
$S^L(1)$	0.435	3.054	1.645	1.712	1.671	1.664	1.701[c]
$S^V(1)$	0.356	1.441	1.634	1.660	1.662	1.663	
I_1^L	17.171	37.365	23.213		28.185	27.865	~29[d]
I_1^V	16.777	32.938	27.626		27.898	27.917	

[a] Exact result.

[b] Adopted value, Table 4.4, Ref. 48.

[c] Calculated from the wave function of Kolos and Wolniewicz (Ref. 49) by Zeiss *et al.* (Ref. 12).

[d] From a DOSD calculation by Zeiss *et al.* (Ref. 12).

imposed as a constraint, the mutual agreement of $S(0)$ calculated in the dipole length and velocity forms and the number of electrons in the system, N, can be used to gauge the goodness of the basis (in RPA, using a complete basis $S^L(0)=S^V(0)=N$ [Ref. 43(a)]) and thus the efficiency of the basis set in representing the continuum. It should also be noted that it is not necessary to calculate the individual excitation energies and oscillator strengths when computing the $S(\mu)$ (n even) sum rules by RPA as well as in higher-order improvements of RPA,[43(b)] since there are closed-form expressions for them obtainable directly from the propagator matrices.

III. H_2

Calculations were carried out initially on H_2 at the equilibrium internuclear distance of 1.4011 a.u. (Ref. 44) and with various standard and expanded basis sets, as given in Table I. In Table II, the values for the $\mu=1$ and 2 oscillator strength sum rules [Eqs. (1) and (2)] and mean excitation energy [Eq. (3)] are presented, calculated in both the dipole length and dipole velocity formulations. It is clear that the reported quantities have converged with respect to basis-set size, and that the results are consistent with accepted values. It is thus not necessary to go beyond RPA to obtain good sum rules. In addition, it appears that the degree of fulfillment of the TRK sum rule is, in addition to a basis-set gauge, also a measure of the goodness of the calculation of I_0.

If one wishes to calculate mean excitation energies of larger systems on a routine basis, it is clear that basis sets of the size equivalent to the 78 or 90 contracted Gaussian-type orbitals (CGTO's) for H_2 are too large, and that useful, smaller bases must be found which will produce results of acceptable quality. One such choice has recently been proposed by Roos and Sadlej.[50] They suggested that basis sets should be extended with functions with the proper functional dependence to describe the property of the one-electron perturbation under consideration. As we consider electric dipole transition matrix elements, this implies that a basis set should contain polarization functions which are derivatives of the primitive set if we compute them in the dipole velocity approximation. In order to test the efficiency of this formulation, we augmented the basis sets 4 and 12 (Table I) with polarization functions produced by taking the derivatives of each contracted function, keeping the contraction coefficients the same. Each s function in the original set thus produces a p polarization function, and each p function produces an s and a d polarization function. Such a procedure produces bases of 16 and 44 CGTO's, respectively, which contain polarization functions with much larger exponents than are normally used. The results of these calculations are presented in Table III.

TABLE III. H_2 oscillator sum rules [$S(1)$ in a.u., I_μ in eV] calculated with basis sets which are designed (Ref. 50) to give optimal results in the dipole velocity formulation.

Basis size (CGTO's)	16	44	
Size of primitive basis (CGTO's)	4	12	
Contracted basis	[2s,2p]	[4s,4p,1d]	
SCF energy (a.u.)	−1.128 362	−1.133 212	Accepted values[a]
$S^L(0)$	2.393	2.020	2000
$S^V(0)$	1.803	1.990	
I_0^L	28.224	20.102	19.2
I_0^V	19.336	19.435	
$S^L(1)$	3.505	2.079	1.701
$S^V(1)$	1.609	1.679	
I_1^L	56.303	50.350	~29
I_1^V	32.282	29.657	

[a] See footnotes of Table II.

As these basis sets are not designed for energy optimization, it is not surprising that the total energies are not competitive with a more conventional basis expansion. It is also clear that the velocity formulation gives much better results than does the length formulation. The re-

TABLE IV. Mean excitation energies (in eV) I_μ $(-2 \le \mu \le 2)$ at $R = 1.4011$ a.u.

	I_2	I_1	I_0	I_{-1}	I_{-2}
This work: 90-*L* basis[a]	65.48	26.57	19.44	16.63	15.30
44-*V* basis[b]	129.86	29.66	19.43	16.62	15.28
	129.71[c]	29.31[c]	19.12[c]	16.35[c]	15.03[c]
Zeiss *et al.*[d]	282.5	29.13	19.26	16.31	14.93
Ford and Brown[e]	44.66[c]	25.39[c]	19.52	16.43[c]	
			19.21[c]		
Others	247.2[f]	31.82[g]	19.5[f]	16.31[h]	
	250[h]		19.2[h,i]	16.28[g]	
			19[i]		
			18.72[j]		
			18.6[k]		
			18.2[l]		

[a] Basis 90, length formulation.
[b] Basis 44, velocity formulation.
[c] Vibrationally average, see text.
[d] Zeiss *et al.*, Ref. 12.
[e] Ford and Browne, Ref. 51.
[f] Garcia, Ref. 52.
[g] Langhoff and Yates, Ref. 8.
[h] Gerhart, Ref. 53.
[i] Ziegler, Ref. 54.
[j] Burger and Seltzer, Ref. 48.
[k] Victor and Dalgarno, Ref. 55.
[l] Kamikawai *et al.*, Ref. 56.

TABLE V. Moments $S(\mu)$ [see Eq. (1); in a.u.] $(-6 \le \mu \le 2)$ for H_2 at $R = 1.4011$ a.u.

	$S(2)$	$S(1)$	$S(0)$[a]	$S(-1)$	$S(-2)$	$S(-3)$	$S(-4)$	$S(-5)$	$S(-6)$
This work: 90-*L* basis[b]	2.510	1.664	2.000	3.054	5.228	9.551	18.174	35.529	70.774
44-*V* basis[c]	3.449	1.679	1.990	3.040	5.211	9.532	18.129	35.309	69.773
From accurate Ψ_0[d]	3.692	1.704		3.097	5.429				
Zeiss *et al.*[e]	3.771	1.676	2.000[f]	3.100	5.478	10.18	19.96		82.94
Victor and Dalgarno[g]	1.56	1.520	2.000[f]	3.135	5.450	10.12	19.63		
Gerhart[h]	3.948	1.670	2.000[f]	3.201[f]	5.428[f]		20.112		78.59
Dalgarno and Williams[i]			2.000[f]				19.6		74.2

[a] Should be 2.000 by TRK sum rule.
[b] Basis 90, length formulation.
[c] Basis 44, velocity formulation.
[d] Calculated from the wave function of Kolos and Wolniewicz (Ref. 49) in Zeiss *et al.* (Ref. 12) and Victor and Dalgarno (Ref. 55).
[e] Zeiss *et al.*, Ref. 12.
[f] Constraint on calculation.
[g] Victor and Dalgarno, Ref. 55.
[h] Gerhart, Ref. 53.
[i] Dalgarno and Williams, Ref. 57.

TABLE VI. Internuclear dependence of I_0 and I_1 for H_2 calculated with basis 44. Calculated in the velocity formulation.

R (a.u.)	$S(0)$	I_0 (eV)	$S(1)$ (a.u.)	I_1 (eV)
1.2011	1.9888	21.4706	1.8529	32.5447
1.3011	1.9893	20.4034	1.7612	30.9992
1.3511	1.9895	19.9074	1.7191	30.3047
1.4011[a]	1.9897	19.4346	1.6794	29.6568
1.4511	1.9899	18.9836	1.6418	29.0519
1.5011	1.9901	18.5534	1.6062	28.4866
1.6011	1.9903	17.7507	1.5406	27.4633
1.8011	1.9905	16.3486	1.4284	25.7761

[a] $R = R_e$.

TABLE VII. Rovibrational averages of I_0 and I_1 for H_2 (calculated with basis 44 in the velocity formulation) in the vibrational ground state.

v	J	I_0 (eV)	I_1 (eV)
0	0	19.1226	29.3067
0	1	19.1129	29.2806
0	2	19.0839	29.2289
Thermal Average[a]		19.1162	29.2947
Static ($R=R_e$)		19.4346	29.6568

[a] $T=300$ K; $F_0(J)=B_eJ(J+1)-\frac{1}{2}\alpha_eJ(J+1)-D_eJ^2(J+1)^2$; molecular constants from Ref. 44; $J=0,2$.

sults, especially of the 44-CGTO basis set, seem quite good, and the set is small enough to be useful.

In Tables IV and V we report I_μ and $S(\mu)$ for various values of μ, and compare them to several literature values.[13] Both of the bases utilized in the present calculation are seen to give results consistent with other calculations for $\mu \leq 1$, but rather poor results for $\mu=2$. This is not unexpected, as the S and L moments and consequently the mean excitation energies weight the high-energy excitations, that is those in the continuum, more heavily as μ increases, and the high-lying excitations are just those that are most poorly represented in this scheme.

The work of Ford and Brown[51] has shown that thermal averaging can lead to changes in calculated mean excitation energies of the order of several tenths of an eV (see Table IV). The internuclear dependence of the mean excitation energies I_0 and I_1 were determined and are presented in Table VI. The vibrational problem was solved using the basis set consisting of 44 CGTO's by the numerical method of Cooley,[58] using experimental molecular potential energy constants.[44] Averages over different rotational states in the ground vibrational state were computed and the results are given in Table VII. As can be seen, vibrational averaging lowers both I_0 and I_1 by ~ 0.3 eV. Thermal averaging over the $J=0,2$ rotational levels gives very little change from the $J=0$ result. Change of this magnitude is consistent with results previously obtained by Ford and Browne.[51] We also predict a very small difference in the mean ionization energy of ortho and para hydrogen; on the order of 0.01 eV.

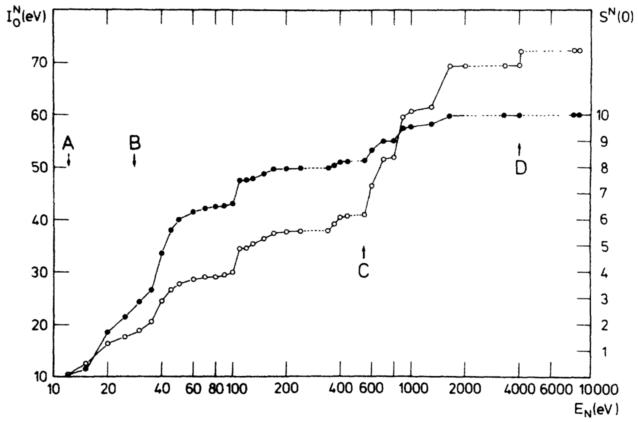

FIG. 1. Accumulation of the Thomas-Reiche-Kuhn sum rule, $S(0)$ (●) and the mean excitation energy I_0 (○) as a function of excitation energy for basis 101 in the length formulation. Dashed line indicates no excitations in this region. A; first ionization potential of H_2O; B; beginning of excitations out of O:2s; C; beginning of excitations out of O:1s; D; beginning of excitations out of O:1s and into Rydberg levels.

These results suggest, then, that reliable mean ionization energies I_μ for H_2 in the range $-2 \leq \mu \leq 1$ can be obtained by first-order (RPA) polarization propagator calculations using Roos-Sadlej-type basis sets, and that I_0 and I_1 should be lowered by ~ 0.3 eV to account for vibrational averaging.

TABLE VIII. Basis sets and SCF energies for H_2O calculations.

Basis number	Primitive basis O	Primitive basis H	Contracted basis O	Contracted basis H	Number of CGTO's	E_{SCF} (a.u.)
14[a]	(9s,5p)	(4s)	(4s,2p)	(2s)	14	−76.009 838
39[b]	(11s,7p,2d)	(5s,1p)	(6s,5p,1d)	(3s,1p)	39	−76.060 784
101[c]	(15s,8p,4d)	(10s,3p)	uncontracted		101	−76.065 283
32[d]	(11s,7p,4d)	(6s,6p)	(5s,3p,1d)	(3s,1p)	32	−76.047 278
44[d]	(11s,7p,4d)	(6s,6p)	(5s,3p,2d)	(3s,2p)	44	−76.054 304
56[d]	(11s,7p,4d)	(6s,6p)	(5s,3p,3d)	(3s,3p)	56	−76.060 842
52[e]	(14s,14p,5d)	(4s,4p)	(6s,6p,2d)	(2s,2p)	52	−76.040 542

[a] The Dunning (Ref. 60) contraction of the Huzinaga (Ref. 45) basis set.

[b] Basis of Lazzeretti and Zanasi (Ref. 61).

[c] Basis of Lazzeretti and Zanasi (Ref. 62).

[d] Bases from Sadlej (Ref. 63), obtained from van Duijneveldt (Ref. 46) primitive basis augmented by polarization functions formed according to Ref. 50. (Orbital exponents and contraction coefficients available from authors on request.)

[e] Basis from Lazzeretti and Zanasi (Ref. 64).

TABLE IX. H_2O oscillator sum rules calculated in the random-phase approximation [$S(0)$ in a.u., I_μ in eV], in both dipole length (L) and dipole velocity (V) formulations.

	Basis set 14	39	101	32	44	56[a]	52	Accepted value
$S^L(0)$	3.609	10.384	10.089	9.409	9.320	9.277	12.664	10.000[b]
$S^V(0)$	2.443	9.228	9.866	9.103	9.170	9.298	8.598	
I_0^L	39.119	69.572	72.463	52.195	56.037	56.508	111.341	71.6[c]; ~60[d]
I_0^V	36.996	73.161	74.156	54.689	57.270	57.685	76.275	
I_1^L	238.625	536.419	923.459	299.692	274.361	283.216	2487.013	931.4[e]
I_1^V	267.488	531.603	898.976	285.139	286.459	296.106	1184.509	

[a]This basis set is optimized to give good results in the mixed dipole-length—dipole-acceleration formulation (Ref. 64).

[b]Exact result.

[c]Adopted value, Table 5.3, Ref. 48.

[d]Fit to experimental vapor data, Ref. 65.

[e]From a DOSD calculation by Zeiss *et al.*, Ref. 12.

IV. H_2O

The calculations on water were all carried out at the standard geometry of $R_{OH}=1.811096$ a.u. and $\theta=104.4489°$.[59] As in the case of H_2, a variety of basis sets was used, and their characteristics are summarized in Table VIII. Of these bases, the first three are of standard construction, while the last four have polarization functions added that are constructed as in the H_2 case as suggested by Roos and Sadlej.[50] In Table IX some of the characteristics of the oscillator strength distributions obtained are given. Of the standard basis sets, basis 101 gives the best agreement between length and velocity results and good agreement with accepted values. We also note that the results in basis 52 are quite poor, which is not surprising since this basis was constructed to give optimal results in the mixed length-acceleration formulation. It is perhaps more unexpected that the Roos-Sadlej bases,[32,34,56,52] designed in the same way as we did for H_2, provide nowhere near the quality as was obtained in the case of H_2. In none of these cases is the TRK sum rule or the mean excitation energy acceptable. This is probably due to the fact that the number of basis functions per electron is nearly a factor of 4 smaller for water than for H_2. This is evidently too serious a reduction for a basis set prepared following the Roos-Sadlej recipe.

In Table X the mean excitation energies I_μ and moments $S(\mu)$ for basis 101 in the length formulation are compared to the semiempirical DOSD results of Ziess *et al.*[12] Agreement is quite good for $-2\leq\mu\leq 1$, but progressively deteriorates (when compared to Ziess *et al.*) for the higher moments. Again, this is not unexpected as errors in the exciton energies enter as the power μ.

It is expected that thermal averaging would lower the value of I_0 for H_2O analogously to the case of H_2. If we allow a decrease of 0.3 eV, as found in H_2, then our best value (basis 101, dipole length formulation) of I_0 is lowered to 72.4 eV, differing less than 1% from the generally accepted[48] value of 71.6 eV and overlapping with it if the ±2% reported uncertainty[48] is considered. It is disturbing that the best available fit to experimental stopping powers of water vapor[65] yields a value some 20% lower than this. It is evident, however, that this work supports the higher value.

In Fig. 1 we present the accumulation of the TRK sum

TABLE X. Mean excitation energies (eV) and moments of the oscillator strength distribution for H_2O calculated in the dipole length formulation with basis 101.

	I_2	I_1	I_0	I_{-1}	I_{-2}
This work[a]	2.13×10^6	923.46	72.46	26.77	19.91
Zeiss *et al.*[b]	1.79×10^4	931.4	71.62	25.00	17.65

	$S(2)$	$S(1)$	$S(0)$	$S(-1)$	$S(-2)$	$S(-3)$	$S(-4)$	$S(-5)$	$S(-6)$
This work[a]	56910	96.10	10.09[c]	7.098	8.499	12.83	22.90	46.62	105.8
Zeiss *et al.*[b]	10610	95.60	10.00[d]	7.316	9.642	16.75	35.42		240.1

[a]I_μ in eV, $S(\mu)$ in a.u.

[b]Zeiss *et al.*, Ref. 12.

[c]This number deviates in the second decimal place from the result of Lazzeretti and Zanasi using the same basis set (Ref. 62), probably due to different machine accuracy. Also, they use a two-electron integral threshold of 10^{-10} a.u. while we have used 10^{-7} a.u. as the threshold in the present calculations.

[d]Constraint on the calculation.

rule $S(0)$ and the mean excitation energy I_0 as a function of excitation energy. We define $S^N(0)$ as the accumulated value of the $S(0)$ moment up to a maximum excitation energy E_N:

$$S^N(0)=\sum_{n}^{E_{0n}<E_N} f_{0n} , \tag{6}$$

where E_{0n} and f_{0n} are the excitation energies and oscillator strengths, respectively. Similarly, we define I_0^N as

$$I_0^N=2R \exp[L^N(0)/S^N(0)] \tag{7}$$

when $L^N(0)$ bears the same relationship to $L(0)$ as $S^N(0)$ does to $S(0)$.

From the figure it can be seen that both I_0 and $S(0)$ have large contributions beginning at each of three excitation thresholds: for excitation out of the oxygen 2s orbital (B), for excitation out of the oxygen 1s core orbital (C), and, smaller, for excitations from the oxygen 1s core to high-lying Rydberg states. This is consistent with the observation[34] that I_0 [and $S(0)$] is primarily determined by the excitation spectrum at intermediate energies. It is also clear from the figure that one must not truncate the excitation spectrum in order to save on computational time.[66] For example, although truncation of the sums [Eqs. (6) and (7)] gives $S^{2000}(0)=9.98$, only 0.2% error, one finds $I_0^{2000}=69.3$ eV, off by 4.5% from the value when the full excitation space is utilized.

V. SUMMARY

The polarization propagator formalism at the RPA level of approximation has been used to calculate the moments of the oscillator strength distribution and the mean excitation energies of H_2 and H_2O. The results for $S(\mu)$ and I_μ are estimated to be reliable to approximately 5% for $-1 \leq \mu \leq 1$, but deteriorate for the higher moments. It is possible to obtain values of I_0, which is both the most accurate and most useful of the mean excitation energies, to approximately 1%, but it appears that rather extended basis sets must be utilized.

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