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Continuum Contributions to Dipole Oscillator-Strength Sum Rules for Hydrogen in Finite Basis Sets

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Abstract

Calculations of the continuum contributions to dipole oscillator sum rules for hydrogen are performed using both exact and basis-set representations of the stick spectra of the continuum wave function. We show that the same results are obtained for the sum rules in both cases, but that the convergence toward the final results with increasing excitation energies included in the sum over states is slower in the basis-set cases when we use the best basis. We argue also that this conclusion most likely holds also for larger atoms or molecules.

1. INTRODUCTION

Many molecular properties are expressed as sums over states; the list includes a range of electric and magnetic properties.^{1,2} Also, the only essential material constant in the simple Bethe theory of stopping of swift

charged particles in matter, the mean excitation energy, is a sum over states.^{3,4} In all cases, the sums run over all excited states of the molecules, discrete, and continuum. Contemporary calculations of electronic structure are nearly all performed using large, but finite, basis sets. Applying sufficiently large basis sets, one may obtain a good description of bound and excited states of an atom or molecule, but, no matter how large and flexible the finite basis set is, one can obtain an only approximate description of the continuum. The continuum contributions to the sum-overstates part of the molecular property hence rely upon a stick-spectrum representation of the true continuum contribution. All experience shows that this approximation works well for a range of molecular sum rules and other properties.^{5,6}

In this paper, we assess the background for this experience by investigating how well the stick-spectrum representation of the continuum contributions works for a number of dipole oscillator-strength sum rules in the simple case of hydrogen; this atom is the only one for which we know the exact continuum wave functions.⁷ By comparing the computed sum rules using both the exact wave functions and a range of finite basis sets, we can thus acquire further insight into the background for the usefulness of the stickspectrum representation of continuum contributions to sum-over-states properties of atoms and molecules.

The purpose of this paper is thus to give an improved understanding of how the convergence toward the exact result for the sum rules—which are known for hydrogen^{8,9}—is obtained when we apply various basis sets as compared to the convergence when using the correct continuum wave function.

We first give a brief summary of the sum rules that we tested. Then follow computational details and we end with the results and a discussion of the implications of our findings.

1.1 Definition of Sum Rules

We consider electric-dipole oscillator-strength sum rules of two kinds,

$$S_{p} = \sum_{n \neq n_{0}} (E_{n} - E_{n_{0}})^{p} f_{nn_{0}} + \int E^{p} \frac{df}{dE} dE$$
(1)

and

$$L_{p} = \frac{dS_{p}}{dp} = \sum_{n \neq n_{0}} (E_{n} - E_{n_{0}})^{p} f_{nn_{0}} ln(E_{n} - E_{n_{0}}) + \int E^{p} ln(E) \frac{df}{dE} dE$$
(2)

Here, n_0 and n index the ground and excited states, respectively; f is the dipole oscillator strength. In both equations, the summation extends over all bound states and the integration is over the continuum. In a calculation with a finite basis set, the integration over the continuum is approximated with a numerical integration in which the integration points are the stick-spectrum representation of the continuum. The integration points are always finite in number but vary with the choice of basis set.

For large negative values of p in Eqs. (1) and (2), the sum rule in essence depends upon only the bound-state spectrum, but, for positive values of p, the continuum contributions to the sum rules dominate; these are the sum rules with which we are primarily concerned in this paper. To be able to monitor the convergence with the number of excited states in the sum over states, we report test calculations for hydrogen using both the exact continuum functions and calculations in a number of finite basis sets.

The Thomas–Reiche–Kuhn (TRK) sum rule¹⁰ is probably the best known S_p sum rule; it states that

$$S_0 = N \tag{3}$$

in which *N* is the number of electrons in the system. The TRK sum rule holds for exact wave functions and in the random-phase approximation (RPA)¹¹; the fulfillment of this sum rule is commonly used as a measure of the completeness of basis sets in basis-set calculations of dipole oscillator-strength sum rules.¹²

Many other sum rules are related to properties of matter. S_{-2} is the static dipole polarizability; S_{-2i} , $i=2, 3, 4 \dots$ can be used to calculate the frequency dependence of the dipole polarizability at low frequencies.¹³ For an atom, S_{-1} is related to the quadrupole moment of the ground state and S_1 is related to the ground-state kinetic energy.⁸

Also, the ratio between the L_p and S_p sum rules

$$I_p = \exp\left(\frac{L_p}{S_p}\right) \tag{4}$$

is of interest in several connections, most prominently in the theory of the stopping power as I_0 , the mean excitation energy, is the only material constant in the simple Bethe theory of stopping.⁴ The broadening of a beam after its passage through a target, in the theory of stopping power referred to as straggling, may be related to the I_1 sum rule.¹⁴

2. COMPUTATIONAL ASPECTS

Exact calculations of sum rules for hydrogen are readily available in the literature. As we seek to study the convergence of the sum rules as a function of the magnitude of excited states included in the sums and integrations in Eqs. (1) and (2), we repeated these calculations using exact wave functions for both bound states and the continuum,⁷ making use of advanced mathematical software (Maple).¹⁵ All those calculations were made with either exact algebraic formulae and arithmetic or floating-point arithmetic (precision at least 13 decimal digits) when exact formulae were impracticable.

Basis-set calculations were performed with the DALTON program package.¹⁶ The full excitation spectrum was generated from the RPA method that for a one-electron system provides the exact solutions within the given basis set. A series of basis sets were tested. We began with the Dunning aug-cc-pVXZ, X=4, 5, and 6, which turned out to be unable to produce correct results for p=1 and 2 sum rules. We had to add both more tight and more diffuse functions to obtain agreement for all sum rules. The final basis set (25s29p) consists of the *s*- and *p*-type functions of Dunning's d-aug-cc-pV6Z basis set augmented with extra tight and diffuse functions: 1s-function (α =18718.77), 11 sets of *p*-functions (α =8.649, 21.805, 54.962, 138.51, 348.99, 879.17, 2214.3, 0.6437, 0.2015, 0.006567, 0.002056), and a set of 12s and 12p continuum-like basis functions as suggested by Kaufman et al.¹⁷ with initial quantum number 1 and terminal quantum number 12. We refer to this basis as the 13s17p+1-1-12 basis set.

3. RESULTS AND DISCUSSION

In Table 1, we report some sum rules for hydrogen calculated using both the exact discrete and continuum wave functions, labeled Exact-Maple, and finite basis-set calculations of both bound and continuum states. In the latter calculation, we used the tailored 13s17p+1-1-12 basis set in both the length and the velocity approximation as it gave the best sum rules in all tested cases. We compare also with the value reported by Inokuti,⁹ which we assume to be correct to the quoted decimal places.

	Length	Velocity	Exact-Maple	Inokuti ^{9a}
S_6	172.19	172.19	172.19	172.19
<i>S</i> ₋₂	4.500	4.500	4.500	4.500
S_{-1}	2.000	2.000	2.000	2.000
S_0	1.000	1.000	1.000	1.000
<i>S</i> ₁	0.667	0.667	0.666	0.667
S_2	1.333	1.319	1.333	1.333
L_0	-0.596	-0.596	-0.596	-0.596
L_1	-0.081	-0.081	-0.082	-0.082
I ₀	14.991	14.991	14.991	14.990

Table 1	Calculated Sum Rules for	r Hydrogen in Atomic	c Units, Except for I ₀ \	Which Is in eV
	Length	Velocity	Exact-Maple	Inokuti ^{9a}

^aInokuti's results in rydberg are converted into atomic units.

From the agreement between the length and velocity results, we conclude that the basis-set results have converged; from a comparison between the last two columns in Table 1, we conclude also that they have converged toward the correct results.

Thus, in this as in many previous applications, the basis-set calculations of the continuum contributions to the dipole oscillator sum rules work well for all values of p in Eqs. (1) and (2). The larger the continuum contributions to the sum rules are, the more care one must take with the choice of basis sets. To obtain a correct value of S_2 for H, it was thus necessary to include both tight basis functions and basis functions tailored to describe Rydberg states and the continuum.¹⁷

We proceed to consider the convergence of the sum rule as a function of the number of excited states included in the summation and integrations in Eqs. (1) and (2); we see whether this convergence differs when we use the basis-set representation of the continuum states or the exact continuum states. This point is illustrated in Figs. 1-8 using our best basis set.

All figures illustrate that there is no perceptible difference in the exact and basis-set calculations of the contributions to the sum rules from the bound states. For the continuum contributions, however, the convergence toward the correct result is slower in the basis-set cases than in the exact case. We thus have a slightly different representation of the continuum in the two



Fig. 1 The S_{-2} sum rule as a function of the excitation energy included in the sum overstates in the exact case (exact) and calculated in dipole length using the best basis set (13*s*17*p*+1-1-12). The *vertical dotted line* marks the onset of the continuum.



Fig. 2 The S_{-1} sum rule as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13s17*p*+1-1-12). The *vertical dotted line* marks the onset of the continuum.



Fig. 3 The S_0 sum rule as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13s17*p*+1-1-12). The *vertical dotted line* marks the onset of the continuum.



Fig. 4 The S_1 sum rule as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13*s*17*p*+1-1-12). The *vertical dotted line* marks the onset of the continuum.

cases, but, eventually, when all excitations are included, the full space is spanned in both cases. Another way of expressing the same conclusion is to state that the intensities of the dipole transitions placed in the continuum are blue-shifted in the basis-set representation, which in turn implies a



Fig. 5 The S_2 sum rule as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13*s*17*p*+1-1-12). Notice the logarithmic scale on the energy axis. The *vertical dotted line* marks the onset of the continuum.



Fig. 6 The L_0 sum rule in atomic units as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13s17p+1-1-12). The vertical dotted line marks the onset of the continuum.



Fig. 7 The L_1 sum rule in atomic units as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13s17*p*+1-1-12). Notice the logarithmic scale on the energy axis. The *vertical dotted line* marks the onset of the continuum.



Fig. 8 The I_0 sum rule in atomic units as a function of the excitation energy included in the sum over states in the exact case (exact) and calculated in dipole length using the best basis set (13s17p+1-1-12). The vertical dotted line marks the onset of the continuum.

slower convergence of a stick-spectrum representation of the continuum contributions. Only when we include all excitation energies in the stick-spectrum representation do we obtain the correct result; that is, only then does the basis set span the same space as the exact continuum wave functions for hydrogen.

One consequence of this behavior of the sum rule as a function of the number of states included in the sum over states is that truncated sum-overstates calculations of properties are not advisable, an issue that has been recognized for many years.¹⁸ Since the convergence of L_0 and S_0 (see Figs. 3 and 6) appears similar for medium continuum excitation energies, one might expect that the ratio of the two sum rule, that is the mean excitation energy (see Eq. 4), might show a faster convergence as a function of the states included in the sum over states. However, Fig. 8 shows that this does not appear to be the case.

The S_p sum rules must increase monotonically with the inclusion of more states in the sum over states as all individual contributions in the sum in Eq. (1) are positive. However, the introduction of the logarithm in the definition of the L_p sum rule (Eq. 2) makes the behavior of L_p as a function of the excitation energy more unpredictable. We see in Figs. 6 and 7 that both L_0 and L_1 go through a minimum a bit above the ionization limit before they attain the monotonic behavior as a function of excitation energy that we saw for S_p sum rules.

We have tested also how the convergence of sum rules are affected by the choice of the basis set. Only in the tailored 13s17p+1-1-12 basis set do we obtain all sum rules correct. We have, however, considered the TRK sum rules for which it is also possible to fulfill Eq. (3) in more modest basis sets. The first test is illustrated in Fig. 9.

Here, we see that the Dunning basis sets show the opposite behavior relative to the exact solution as a function of the excitation energy as does the 13s17p+1-1-12 basis set. For low-lying continuum states the basis set results lie above the exact curve. The lack of agreement for the discrete part of the spectrum indicates, however, that these basis sets give a somewhat random representation of the discrete excitation spectrum and must be considered less reliable for more general sum-over-states calculations of properties.

The same conclusion holds when we work with the pure *sp*-basis sets as we see from the comparisons in Fig. 10.

Only when we include the basis functions tailored by Kaufmann et al.¹⁷ to describe the continuum and Rydberg states do we obtain an effective description both of the bound states and of all sum rules.



Fig. 9 The S_0 sum rule for the aug-cc-pVXZ, X = 4, 5, and 6 basis sets as a function of the excitation energy included in the sum over states. The *vertical dotted line* marks the onset of the continuum.



Fig. 10 The S_0 sum rule for a series of tailored basis sets (see text) as a function of the excitation energy included in the sum over states. The *vertical dotted line* marks the onset of the continuum.

4. CONCLUSION

Using both the stick-spectrum representation of the continuum and the exact continuum wave functions, we show how the convergence with excitation toward the correct results for the S_p and L_p sum rules proceeds for hydrogen, the only example for which it is possible to do both. Both procedures converge toward the same result, but the stick spectrum in the best basis-set representation shows a slower convergence pattern than does the one using the exact wave functions. Other convergence patterns toward the correct results are found in less accurate basis sets.

There is no reason to believe that the specific result for hydrogen cannot be generalized to larger and more complicated atoms and molecules. The main reason for that belief is that, for the high-lying continuum states that give the dominant contributions to the high-*p* sum rules, the continuum is little affected by the actual form of the molecular and atomic structure.

We thus conclude that the test calculations on hydrogen yield adequate reason to believe that the widely applied procedure of approximating the continuum contributions with a stick-spectrum representation is able to produce as accurate results for dipole oscillator sum rules as if we were using a more correct continuum wave function, provided that the basis set is carefully chosen and balanced and that we do not truncate in the sum over states.

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