Approximate sum rule for diatomic vibronic states

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The simple expression $\langle v'|f\Delta U^n g|v'\rangle$ is offered to approximate sums of the form $\sum_{v''=0}^{\infty}\langle v'|f|v''\rangle\langle v''|g|v'\rangle(E_{v'}-E_{v''})^n$, where f and g are some operators which couple the vibrational levels v' and v'' of two interacting electronic states and $\Delta U = U'-U''$ is the difference of the corresponding internuclear potentials. The rigorous quantum proofs as well as semiclassical justification of this formula are presented and its absolute accuracy is estimated in a closed functional form. Invariant properties and spectroscopic applications of the sum rule, including the evaluation of lifetimes, fine-structure (Λ-doubling) constants, and Landé factors, are discussed.

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I. INTRODUCTION

A large part of the computational effort in practical applications of molecular-spectra theory requires the numerical estimation of perturbation-theory series [1,2]. In particular, in the case of a diatomic molecule, when Green's functions cannot be represented in a compact form, one has to use the spectral decomposition of the resolvent and to estimate the series of the following form:

$$S(v',f,g,n)=\sum_{v''=0}^{\infty}\langle v'|f|v''\rangle\langle v''|g|v'\rangle(E_{v'}-E_{v''})^n ,$$

(1)

where $|v'\rangle$ and $|v''\rangle$ are the vibrational eigenfunctions of two different electronic states, $E_{v'}$ and $E_{v''}$ are the corresponding eigenvalues, f and g are some operators, and n is an integer. Note that in standard perturbation theory n is equal to -1 or -2. The case when $n=3$ and $f=g$ is the transition electronic dipole-length moment μ is met in the evaluation of the lifetime of the excited vibrational state v'. The other possible way to estimate the lifetime corresponds to $n=1$ and $f=g=\pi$, where π is the dipole-velocity moment. These examples demonstrate the prime importance of the methods for straightforward evaluation of the sum (1).

The direct evaluation of the sum (1) is a poor method, especially for nondiagonal bound-bound and free-bound transitions, where the well-known closure condition $\sum_{v''=0}^{\infty}\langle v'|v''\rangle^2=1$ requires knowledge of a large number of $|v''\rangle$ wave functions. Obviously, it is a very tedious problem itself. Moreover, the errors of numerical calculation of each term in the sum (1) may introduce a great overall error in the final S value.

The more clever way to handle Eq. (1) is to find an analytical approximation to S, which does not involve the set $|v''\rangle$ at all. Two trivial examples of such a closed relation are

$$S(v',f,g,0)=\langle v'|fg|v'\rangle ,$$

(2a)

$$S(v',f=\text{const},g=\text{const},2)=fg\langle v'|\Delta U^2|v'\rangle ,$$

(2b)

where $\Delta U = U'-U''$ is the difference potential of two interacting electronic states. Although there are no exact generalizations of Eq. (2) for arbitrary f and g operators and n values, its approximate counterpart still can be obtained. This fact is nicely illustrated by the famous Tellinghuisen formula [3,4] for the excited-state lifetime:

$$\tau_{v'}^{-1}\approx\langle v'|\Delta U^3\mu^2|v'\rangle .$$

(3)

Numerical experiments [3,5] demonstrate the high accuracy of Eq. (3) ($\approx 0.2\%$). The classical and quantum analytical proofs for this formula are discussed in Refs. [4,6]. Obviously, in this case the decay channel v'' will be allowed only if the evident condition $E_{v'}>E_{v''}$ is fulfilled. However, the summation might be extended to all v'' without significant loss of accuracy if the characteristic frequencies of electronic transitions Ω are significantly higher than the vibrational frequencies ω [3,5].

In present work we show that Eq. (3) is a particular case of a fairly general closed relation for the sums $S(v',f,g,n)$. Namely, we prove that for arbitrary f, g, and n, the exact sum S can be partitioned as $S\approx S_0+S_1$, where

$$S_0=\langle v'|f\Delta U^n g|v'\rangle$$

(4)

and S_1 is a small correction. An explicit expression for S_1 is also derived under some additional assumptions in Sec. II. This makes possible a straightforward test of the accuracy of approximating the sum S by S_0. A semiclassical interpretation of the formula for S_0 and S_1 is given in Sec. III. Invariant properties as well as important spectroscopic implementations of the sum rule are discussed in Sec. IV.

II. QUANTUM APPROACH

Let us consider a diatomic molecule with internuclear distance q. It is a standard simplification to suppose $q\in(-\infty,+\infty)$ instead of $q\in(0,+\infty)$. For momentum p obeys the usual commutation relation which can be written by Poisson brackets: $\{q,p\}=1$. Hereafter we use atomic units.

Let U' and U'' be the adiabatic potential functions of

two electronic states (U' corresponds to the upper state). v' and v'' symbolize vibrational levels. For a given level v' it is useful to write down the vibrational Hamiltonian H for the upper state as $H = p^2/2m + U' - E_{v'}$. In terms of the difference potential the Hamiltonian of the lower electronic state is equal to $H - \Delta U$, and its spectral resolution is

$$(\Delta U - H)^n = \sum_{v''=0}^{\infty} |v''\rangle (E_{v'} - E_{v''})^n \langle v''| . \tag{5}$$

This representation allows us to rewrite sum (1) in a form independent of v'', i.e..,

$$S(v', f, g, n) = \langle v'|f(\Delta U - H)^n g|v'\rangle . \tag{6}$$

In principle, expression (6) can already be used for an exact evaluation of S. Nevertheless, we will try to transform it into an approximate form (4), which is much simpler to use in practice than direct numerical calculations of the sum S.

To estimate the orders of the considered magnitudes it is useful to have a simple model for the system studied. Let ω' and ω'' denote the vibrational frequencies of the upper and lower electronic states, $E_{v'} = \text{const} + \omega'(v' + \frac{1}{2})$, and the minima of the adiabatic potentials are shifted from each other by δ.

Recall that $\omega', \omega'' \ll \Omega$ where Ω is the mean value of $E_{v'} - E_{v''}$. In other words, $\Omega \approx \Delta U$, when the ΔU value is taken in the region of localization of the wave function $|v'\rangle$ and the adjoint functions $f|v'\rangle$ and $g|v'\rangle$. Note that usually f and g are sufficiently smooth functions on q. This is a typical situation for application of the adiabatic approximation when electronic states are well separated. This model should be acceptable to make real estimations of different corrections.

Under the conditions given above it is reasonable to suppose that the mean value of $H/\Delta U \ll 1$ and to use a power series "in $H/\Delta U$" to estimate S. Then, retaining only the terms linear and zero order in H, we obtain the following approximation for S with positive n:

$$(\Delta U - H)^n \approx \Delta U^n - \sum_{k=0}^{n-1} \Delta U^k H \Delta U^{n-k-1} . \tag{7}$$

The analogous approximation for $n < 0$ can be worked out with the help of the recurrence relation

$$(\Delta U - H)^{-1} = \Delta U^{-1} + \Delta U^{-1} H \Delta U^{-1}$$
$$+ \Delta U^{-1} H (\Delta U - H)^{-1} H \Delta U^{-1} . \tag{8}$$

The largest term ΔU^n in Eq. (7) immediately gives the estimate (4) for the sum S. The other part of the right-hand side of Eq. (7) represents the correction S_1 to S_0. We can suppose that the $S \approx S_0 + S_1$ approximation has an error of the order of $(\omega' + \omega''/2\Omega)^2$.

An explicit derivation of the closed formula for S_1 involves a number of exact commutation relations. We now work out some of them for later use in the S_1 calculation.

Let X and Y be the Hermitian operators which commute with the potential functions, whereas in other respects they are arbitrary functions of the q coordinate

and p momentum. Denoting $\{X, p\}$ as X' and $\{Y, p\}$ as Y', we may formulate the main result as the following lemma.

Lemma:

$$2XHY = (HXY + XYH) + (X'Y')/m$$
$$+ (CqH - HqC) + (qHC - CHq) , \tag{9}$$

where $C = (X'Y - XY')/2$.

Proof: From the definition of X' and the standard properties of the Poisson brackets one has

$$XH = HX + i\{X, H\} = HX + (i/2m)\{X, p^2\}$$
$$= HX + (i/2m)(X'p + pX') . \tag{10}$$

The definition of Y' and the analogous relation for HY immediately yield

$$2XHY = (XH)Y + X(HY)$$
$$= (HXY + XYH)$$
$$+ (i/2m)(pX'Y - XY'p + X'pY - XpY') . \tag{11}$$

It is evident that $X'pY = X'Yp - iX'Y'$. An analogous reorganization of XpY' gives

$$2XHY = (HXY + XYH) + (X'Y')/m$$
$$+ (i/2m)(Cp + pC) . \tag{12}$$

Substitution of the simple relation $p/m = \{q, H\}$ to the last term of Eq. (12) proves the lemma.

Corollary: If $\langle v'|qHC|v'\rangle$ is real, then

$$\langle v'|XHY|v'\rangle = \langle v'|X'Y'|v'\rangle/2m . \tag{13}$$

Proof: From the definition of the Hamiltonian $H|v'\rangle = 0$ and according to the lemma, we have

$$\langle v'|XHY|v'\rangle = \langle v'|X'Y'|v'\rangle/2m$$
$$+ \langle v'|qHC - CHq|v'\rangle/2 . \tag{14}$$

The proof is finished, since the last term on the right-hand side of Eq. (14) is the imaginary part of $\langle v'|qHC|v'\rangle$.

For practical use of the above corollary the wave function $|v'\rangle$ of the vibrational state should be real. For real functions X and Y the C operator is also real and the corollary is true. In the case of complex functions X and Y the proof can be realized for the real and imaginary parts of each function separately. In all cases $C = 0$, when $X = Y$.

Now it is easy to calculate the S_1 correction. Indeed, according to Eq. (7) and for the case $n \geq 0$ we have

$$S_1 = -\sum_{k=0}^{n-1} \langle v'|(f\Delta U^k)H(\Delta U^{n-k-1}g)|v'\rangle , \tag{15}$$

where each term of the sum can be evaluated with the help of the corollary. If f and g are multiplicative functions of q, a simple calculation leads to

$$S_1 = -\langle v'|n\Delta U^{n-1}f'g' + n(n-1)\Delta U^{n-2}\Delta U'(fg)'/2$$
$$+ n(n-1)(n-2)\Delta U^{n-3}(\Delta U')^2 fg/6|v'\rangle/2m , \tag{16}$$

where $\Delta U'$, f', and g' denote the first derivatives of ΔU, f, and g functions, respectively. The relation for $n < 0$ may be easily proved by use of the corollary and the recursion (8). It can be shown that the case $n < 0$ is described by the same formula (16). This fact can be considered as the result of analytical continuation.

For the model introduced above the S_1 value has the form

$$|S_1/S_0| = |n(n-1)(n-2)\delta^2(\omega' + \omega''/2\Omega)^3/24| . \quad (17)$$

Therefore, when $|n| \leq 3$ and δ is equal to a few angstroms, the relative error is small even for the case $(\omega' + \omega''/2\Omega) \approx 0.1$. It is also possible to evaluate the next correction to S. Tedious calculations which rely upon the same basic idea show that in the expansion $S \approx S_0 + S_1 + S_2$ the S_2/S_1 ratio has the order of $v'(\omega' + \omega''/2\Omega)$. Obviously, this correction is negligible in a typical situation of not too large v' values and $\omega', \omega'' \ll \Omega$. Hence, the approximations $S \approx S_0 + S_1$ are accurate enough for common application.

Now we turn to a slightly generalized form of the sums (1) which is useful for some purposes. Let $v'_1 = v'$, $v'_2 \neq v'$, and

$$\tilde{S} = \sum_{v''=0}^{\infty} \langle v'_1|f|v''\rangle\langle v''|g|v'_2\rangle(E_{v'_1} - E_{v''})^n . \quad (18)$$

This expression can be analyzed by the methods developed above. Obviously, $\tilde{S} \approx \tilde{S}_0 + \tilde{S}_1$, where $\tilde{S}_0 = \langle v'_2|f\Delta U^n g|v'_1\rangle$. The formula for $\tilde{S}_1$ follows from the lemma and Eq. (7). In our notations it is easy to see that

$$\langle v'_2|XHY|v'_1\rangle = \langle v'_2|X'Y'|v'_1\rangle/2m$$
$$+ (E_{v'_2} - E_{v'_1})\langle v'_2|XY|v'_1\rangle + \eta , \quad (19)$$

where the form of η is considered later. For a nondiagonal element of the same operator the first term on the right-hand side of Eq. (19) gives the contribution in $\tilde{S}_1$ of the same form as S_1 in Eq. (15). The additional contribution arising from the second term has the value

$$n(E_{v'_2} - E_{v'_1})\langle v'_2|f\Delta U^{n-1}g|v'_1\rangle/4 , \quad (20)$$

which can be estimated as $n(v'_2 - v'_1)(\omega'/\Omega)\tilde{S}_0/4$. Thus, corrections to the "nondiagonal" sums $\tilde{S}_0$ are small only if the difference between v'_2 and v'_1 is small.

The term η generates a contribution in $\tilde{S}_1$ which consists of the matrix elements of the $T = n\Delta U^{n-1}(f'g - g'f)/4$ operator. Note that the terms of Eq. (15) containing the $\Delta U'$ function cancel each other under the summation in Eq. (15). In particular, these terms vanish if $f = g$, whereas in the general situation η contributes to $\tilde{S}_1$ as

$$\langle v'_2|qHT - THq|v'_1\rangle - (E_{v'_2} - E_{v'_1})\langle v'_2|qT|v'_1\rangle . \quad (21)$$

We do not intend to evaluate Eq. (21) in a general form. Instead, we simply estimate it in the harmonic approxi-

mation. In this case, $q|v'\rangle$ can be expressed as a contribution of $|v'\pm 1\rangle$ functions. Then, the largest contributions to Eq. (21) cancel each other and the final expression is a combination of four terms of the form $\sqrt{(v'_2\omega'/m)}\langle v'_2|T|v'_1\rangle$, where v'_2 should be replaced by $v'_2\pm 1$ and v'_1 by $v'_1\pm 1$, respectively.

In all cases these corrections are less by the order of magnitude than the terms of Eq. (16) containing f' and g' functions. The above consideration shows that $\tilde{S} \approx \tilde{S}_0$ and the main corrections are given by Eqs. (16) and (20). This approximation becomes too crude at large $|v'_2 - v'_1|$ values. It is easy to generalize the present derivation for sums of the type (18) which have $E_{v'_2}$ and $E_{v'_1}$ on the right-hand side. Again, the main result is similar to that given before, namely, the closer to zero the difference $v'_2 - v'_1$ is the better the $\tilde{S} \approx \tilde{S}_0$ approximation. In this sense the diagonal case $v'_2 = v'_1$ is the best one.

III. SEMICLASSICAL APPROACH

Now we demonstrate another way to obtain the approximations to S. Recalling the trivial exact relation $E_{v'} - E_{v''} = \langle v''|\Delta U(q)|v'\rangle/\langle v''|v'\rangle$ [7] and expanding ΔU, f, and g functions in power series on $r = q - q'_e$ one has

$$(E_{v'} - E_{v''})^n = \left\{\sum_{k=0}^{\infty} (1/k!)\Delta U_k r_{k,v',v''}\right\}^n , \quad (22a)$$

$$\langle v''|f|v'\rangle = \left\{\sum_{k=0}^{\infty} (1/k!)f_k r_{k,v',v''}\right\}\langle v''|v'\rangle , \quad (22b)$$

$$\langle v''|g|v'\rangle = \left\{\sum_{k=0}^{\infty} (1/k!)g_k r_{k,v',v''}\right\}\langle v''|v'\rangle , \quad (22c)$$

where $r_{k,v',v''}$ is defined as

$$r_{k,v',v''} = \langle v''|r^k|v'\rangle/\langle v''|v'\rangle \quad (23)$$

and the k index marks the kth derivative with respect to q. Multiplication of the series (22) by each other yields the sum (1). On the other hand, multiplying the corresponding power series and substituting the result in integral expression (4), it is easy to estimate the S_0 value. Then, after subtraction of these series from each other we find that the terms with $k = 0, 1$ vanish. Moreover, all the members of the series with $k = 2$ and some with $k = 3$ vanish also due to the relation

$$\sum_{v''=0}^{\infty} r_{m,v',v''}r_{l,v',v''}\langle v''|v'\rangle^2 = \langle v'|r^{m+l}|v'\rangle \quad (24)$$

being valid for all m and l. It follows from the completeness of the $|v''\rangle$ set. Tedious analytical calculations show that the main part of the S_1 correction function has the form

$$S_1 = [n\Delta U_0^{n-1}\Delta U_1 f_1 g_1 + n(n-1)\Delta U_0^{n-2}\Delta U_1^2(f_1 g_0 + f_0 g_1)/2 + n(n-1)(n-2)\Delta U_0^{n-3}\Delta U_1^3 f_0 g_0/6]$$

$$\times \left[\sum_{v''=0}^{\infty} \langle v''|r|v'\rangle^3/\langle v''|v'\rangle - \langle v'|r^3|v'\rangle \right] . \tag{25}$$

It is easy to see that the expressions (25) are similar to Eq. (16). Under the r-centroid approximation [8], the value of $(\langle v''|r|v'\rangle/\langle v''|v'\rangle)^3$ is equal to $\langle v''|r^3|v'\rangle/\langle v''|v'\rangle$. As it follows from Eq. (24) (for the case $m=3$, $l=0$) the value in last parentheses of Eq. (25) vanishes. Thus, the equality $S=S_0$ is exact under the r-centroid approximation. It is interesting to note that application of the stationary phase method [9] for evaluation of the corresponding integrals in Eq. (1) immediately gives

$$S \approx \sum_{v''=0}^{\infty} \sum_{q^*} f(q^*)g(q^*)[\Delta U(q^*)]^n \langle v''|v'\rangle^2 \approx S_0 , \tag{26}$$

where q^* are the stationary points of the phase. This formula can also be considered as a variant of the mean-value theorem. In all cases we can see that the accuracy of an approximation $S\approx S_0$ is at least of the same order as the accuracy of the r-centroid or asymptotic approximations of WKB type. This gives us an additional argument for using the simple formula instead of the much more tedious calculations.

IV. DISCUSSION

The approximation of the sum S as S_0 has noteworthy features. It is invariant with respect to the following transformations:

$$S_0(v',f,g,n) = S_0(v',f\Delta U^k, g\Delta U^k, n-2k) , \tag{27}$$

$$S_0(v',f,g,n) = S_0(v',fa^k, ga^{-k}, n) , \tag{28}$$

where k is an arbitrary number and $a(q)$ is an arbitrary function of the q coordinate. In contrast to S_0, both S and S_1 functions are affected by these transformations. It is therefore instructive to analyze the behavior of the S_1 correction function. For instance, applying the transformations (27) and (28) to Eq. (16) for the case $k=1$, we find that the corresponding changes of the S_1 function have the following forms:

$$\Delta S_1 = \langle v'|2\Delta U^{n-1}f'g' + (n-1)\Delta U^{n-2}\Delta U'(fg)'$$
$$+ (n-2)(n-3)\Delta U^{n-3}(\Delta U')^2 fg|v'\rangle/2m , \tag{29}$$

$$\Delta S_1 = \langle v'|n\Delta U^{n-1}[(a'/a)(f'g - fg')$$
$$- (a'/a)^2(fg)]|v'\rangle/2m . \tag{30}$$

It is clear from Eqs. (29) and (30) that for slowly varying f' and g' functions the absolute variations of the S_1 and S functions increase as $(n-2)(n-3)$ and n, respectively.

We consider this fact in more detail in connection with the lifetime estimation. In this case ($n=3$ and $f=g=\mu$), from Eq. (16) we have

$$S_1^{\mu} = -\langle v'|3(\mu')^2\Delta U^2 + 6\mu\mu'\Delta U'\Delta U + (\Delta U')^2\mu^2|v'\rangle/2m . \tag{31}$$

It is interesting to compare S_1^{μ} with the S_1^{τ} value obtained for $n=1$ and $f=\pi^*$, $g=\pi$, since the $S^{\tau}=S_0^{\tau}+S_1^{\tau}$ representation is exact. Here $\pi=\Delta U\mu$ defines the transition moment in the momentum (dipole-velocity) representation. In this case, we have (see also Ref. [6])

$$S_1^{\tau} = -\langle v'|(\pi')^2|v'\rangle/2m$$
$$= -\langle v'|(\mu')^2\Delta U^2 + 2\mu\mu'\Delta U'\Delta U + (\Delta U')^2\mu^2|v'\rangle/2m . \tag{32}$$

Therefore, if the first derivative of the μ function is negligible in comparison with $\Delta U'$, then $S_1^{\mu}\approx S_1^{\tau}$. On the contrary, if $\Delta U\approx$ const, while μ is varied strongly, then $S_1^{\mu}\approx 3S_1^{\tau}$. It should be emphasized that the same result follows directly from Eq. (29). Indeed, at $n=3$ we obtain

$$S_1^{\tau} - S_1^{\mu} = \langle v'|\Delta U^2(\mu')^2 + \Delta U\Delta U'(\mu^2)'|v'\rangle/m . \tag{33}$$

Now we summarize some other spectroscopic applications of the suggested sum rule including the effects of regular perturbations on fine-structure (Λ-doubling) constants and Landé factor values. For electronic perturbation parameters describing the shifts and splittings of the Λ-doublet components of a Π state caused by interactions with $\Sigma^{\pm}$ states of the same multiplicity [10] we find

$$o_{v'}^{\Pi} = S(v',AL_+,AL_+,-1)/4 \approx \langle v'|(AL_+)^2/\Delta U|v'\rangle/4 , \tag{34a}$$

$$p_{v'}^{\Pi} = 2S(v',AL_+,BL_+,-1) \approx 2\langle v'|AB(L_+)^2/\Delta U|v'\rangle , \tag{34b}$$

$$q_{v'}^{\Pi} = 2S(v',BL_+,BL_+,-1) \approx 2\langle v'|(BL_+)^2/\Delta U|v'\rangle . \tag{34c}$$

For Landé factors of $\Sigma^{\pm}$ states originating from interaction with paramagnetic Π states [11] we have

$$g_{v'}^{\Sigma} = 2S[v',(A+2B)L_+,L_+,-1]$$
$$\approx 2\langle v'|(A+2B)(L_+)^2/\Delta U|v'\rangle . \tag{35}$$

V. CONCLUSIONS

Based on simple commutation relations we have obtained the approximate sum rule $S(v',f,g,n) \approx \langle v'|f\Delta U^n g|v'\rangle + S_1$, where S_1 is given by formula (16). This estimation requires greatly reduced information about a second electronic state, namely, only a knowledge of the potential curve of this state. Formulas for S_1 functions have been found for the case of multiplicative f and g operators on the same coordinate. However, it is also valid in some other cases: (a) In multidimensional problems when Hamiltonians have the form

$\sum_i p_i^2/2m_i + U$, an additional summation over i appears. (b) If f and g are arbitrary operators, f' in Eq. (16) should be replaced by $\{f,g\}$ and estimation of the $\{f,U'\}$ value is also needed. (c) The expression (16) estimates the S_1 correction with an additional error of the order of $nm\omega S_0/\Omega$, when the sum (1) corresponds to v' differing by the integer m.

The relations of type (4) are strongly recommended for implementation in calculations of lifetimes, Λ constants, and Landé factors of excited states, even if S_1 corrections are neglected in the consideration. We hope that the proposed sum rule will prove to be useful for qualitative estimations as well as quantitative evaluations of other diatomic properties, such as electronic parts of polarizability and high-frequency terms of magnetic susceptibility.

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