Upper and lower bounds to quantum-mechanical sum rules

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F. WEINHOLD†
Mathematical Institute, Oxford
MS. received 17*th June* 1968

Abstract. It is pointed out that when a set of sum rules $S(k)$ are composed into an array S with elements $S_{ij} = S(i+j)$, the resulting matrix S has no negative eigenvalues. This property often permits one to give rigorous upper and/or lower bounds to the true value of a particular sum rule when values of other sum rules are known. In certain cases the bounds are identical with those obtained recently by Gordon using a generalized theory of Gaussian integration. The technique is illustrated by an application to oscillator strength sum rules in the ground state of the hydrogen atom and the negative hydrogen ion, and finally it is shown how any available information about individual oscillator strengths can be applied to further improve the bounds.

1. Introduction: positivity of the metric matrix

For the determination of upper and lower bounds to sum rules it is useful to appeal to some elementary notions of geometry in n-dimensional Euclidean vector spaces, and we accordingly review some basic results for the sake of completeness.

It is often profitable to regard objects $|a_i\rangle$ as *vectors* whenever it is possible to define a scalar product $\langle a_i|a_j\rangle$ having the following fundamental properties:

$$\langle a_i|a_j\rangle = \langle a_j|a_i\rangle^* \tag{1.1a}$$

$$\langle a_i|\alpha a_j+\beta a_k\rangle = \alpha\langle a_i|a_j\rangle+\beta\langle a_i|a_k\rangle \tag{1.1b}$$

$$\langle a_i|a_i\rangle \geqslant 0. \tag{1.1c}$$

It will then be possible to represent the $|a_i\rangle$, $i = 1, 2, ..., n$, as ordinary column vectors in a Euclidean space E_n of n dimensions, and to manipulate them according to familiar rules.

Consider the matrix A whose columns are the vectors $|a_1\rangle, |a_2\rangle, ..., |a_n\rangle$. Then the *metric* (overlap) matrix S with elements $(S)_{ij} = \langle a_i|a_j\rangle$ may be written in the form

$$S = A^\dagger A \tag{1.2}$$

where $A^\dagger$ is the Hermitian adjoint of A. From the form of (1.2) it is clear that the metric matrix is positive (semi-) definite, since, for *any* vector $|x\rangle$,

$$\langle x|S|x\rangle = \langle x|A^\dagger A|x\rangle = \langle Ax|Ax\rangle \geqslant 0$$

according to (1.1c). Thus S certainly has no negative eigenvalues and, in particular,

$$G = \det|S| \geqslant 0 \tag{1.3}$$

where G is also called the *Gramian* determinant (see, e.g., Bellman 1960, p. 46) of the vectors $|a_i\rangle$. G is actually the squared volume of the parallelopiped spanned by the vectors $|a_i\rangle$, and, hence, is clearly non-negative, being zero only when the vectors become linearly dependent.

Since the positivity of the metric matrix is the necessary and sufficient condition for the *existence* of vectors having the required lengths and inner products, it is the *strongest possible* restriction that can be placed on the value of any one matrix element if the only information available is given by the values of the other matrix elements of S.

2. Application to sum rules

For the application to *sum rules* $S(k)$ (see, e.g., Hirschfelder *et al.* 1964)

$$S(k) = \sum_{n=1}^{\infty} f_{0n}(E_n - E_0)^k \tag{2.1}$$

we may assume for specificity that the N-electron system described by $H\psi_i = E_i\psi_i$ is perturbed in its ground state by an external electric field, so that f_{0n} is the familiar oscillator strength for dipole transitions from state ψ_0 to state ψ_n

$$f_{0n} = \tfrac{2}{3}(E_n - E_0)|\langle\psi_0|\sum_{i=1}^{N} \boldsymbol{r}_i|\psi_n\rangle|^2 \tag{2.2}$$

though it will be clear that the application to other types of perturbation is immediate. The summation sign in (2.1) denotes summation over the discrete states and an integration over the photoionization continuum.

The oscillator strengths are intrinsically positive, and for our purposes it is only necessary to remark that (2.1) may be written in the form (see also Gordon 1968 b, c)

$$S(k) = \int_{\omega_1}^{\infty} \omega^k \phi(\omega)\, \mathrm{d}\omega \tag{2.3}$$

where the *distribution function* $\phi(\omega)$ is non-negative and where $\omega_i \equiv E_i - E_0$. We may then formally introduce the function $\chi(\omega)$ satisfying $\chi^*(\omega)\chi(\omega) = \phi(\omega)$ and adopt the integral (2.3) as the scalar product for the system of 'vectors' $\omega^n|\chi\rangle$

$$\langle\omega^n\chi|\omega^m\chi\rangle = \int_{\omega_1}^{\infty} \chi^*(\omega)\omega^{n+m}\chi(\omega)\, \mathrm{d}\omega = S(n+m) \tag{2.4}$$

which has all the properties required by (1.1*a–c*). Thus, according to (2.4), the metric matrix S of this system is just an array of sum rules, and the non-negativity of this array will impose upper and/or lower bounds on the numerical value of any particular $S(k)$ if values are known for all other elements of the sum rule array.

Actually the positivity of the array S

$$(S)_{ij} = S_{ij} = S(i+j)$$

may be directly established without referring to any properties of the square root function χ, since

$$\langle x|S|x\rangle = \sum_i \sum_j x_i x_j S_{ij} = \sum_i \sum_j x_i x_j \int \omega^i \omega^j \phi(\omega)\, \mathrm{d}\omega$$

$$= \int \mathrm{d}\omega\, \phi(\omega)|\sum_i x_i\omega^i|^2 \geqslant 0$$

but it is often useful to keep the geometrical argument in mind.

3. Explicit formulae for simple cases

The simplest of our bounds, corresponding to a 2×2 metric matrix, is the Schwarz inequality†

$$S_{ii} \geqslant S_{ij}^2/S_{jj}$$

where we have again used the notation $S_{ij} = S(i+j)$ for the sum rules. In all the formulae of this section the indices $i, j, k, \ldots$ will be understood to be *all* integer or *all*

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† For $i = -1, j = 0$ this inequality is closely related to the *Kirkwood–Vinti* approximation to the polarizability (Kirkwood 1932, Vinti 1932), since S_{ij} then becomes simply the number of electrons according to the Thomas–Reiche–Kuhn sum rule.

half-integer, so that $i+j$ is always an integer, but of course this restriction may be omitted if non-integer sum rules are of interest.

For the 3×3 Gramian

$$G = \begin{vmatrix} S(2i) & S(i+j) & S(i+k) \\ S(i+j) & S(2j) & S(j+k) \\ S(i+k) & S(j+k) & S(2k) \end{vmatrix} \geqslant 0$$

one obtains for the diagonal element $S(2i) = S_{ii}$ the lower bound

$$S_{ii} \geqslant \frac{S_{jj}S_{ik}{}^2 + S_{kk}S_{ij}{}^2 - 2S_{ij}S_{ik}S_{jk}}{S_{jj}S_{kk} - S_{jk}{}^2} \tag{3.1}$$

while for the off-diagonal element S_{ij} solution of the quadratic equation $G = 0$ gives the upper and lower bounds

$$S_{ij} \gtrless \frac{S_{ik}S_{jk} \pm \{(S_{ii}S_{kk} - S_{ik}{}^2)(S_{jj}S_{kk} - S_{jk}{}^2)\}^{1/2}}{S_{kk}}. \tag{3.2}$$

Finally for the case $i+k = 2j$, where the element to be bounded occurs three times in the matrix S, upper and lower bounds for S_{ik} are found as the roots of the cubic equation $G = 0$. First find the two *largest* roots x_α, x_β of the equation

$$f(x) = x^3 - x(2S_{ij}S_{jk} + S_{ii}S_{kk}) + (S_{ii}S_{jk}{}^2 + S_{kk}S_{ij}{}^2) = 0. \tag{3.3a}$$

Then the bounds are

$$x_\alpha \geqslant S_{ik} \geqslant x_\beta. \tag{3.3b}$$

The 4×4 array requires values of from 6 to 9 of the $S(k)$ and will therefore be of more limited general applicability. The upper/lower bounds are obtained as solutions of the linear, quadratic, cubic, or quartic equation $G = 0$ according to the number of times the element to be bounded appears in G. Since it may be computationally more convenient to obtain these roots numerically, the explicit formulae are not included here, although an application is presented in § 5.

4. Gordon's error bounds

Recently Gordon (1968 a, b, c) has developed a powerful set of techniques based on the generalized theory of Gaussian integration for determining error limits to various quantum- and statistical-mechanical properties. Of particular interest for our purposes is his treatment of the second-order perturbation energies (Gordon 1968 b) and the associated long-range (van der Waals–London dispersion) forces between atoms (Gordon 1968 c).

In Gordon's approach one considers a certain *positive* distribution $\phi(u)$ and the associated *moments* μ_k defined by

$$\mu_k = \int u^k \phi(u) \, du.$$

Then the quantity of interest $I = \int f(u)\phi(u) \, du$, where f is a known function, is approximated by the M-point quadrature formula

$$I = \int f(u)\phi(u) \, du = \sum_{i=1}^{M} w_i f(\xi_i) + R$$

where the remainder term R actually vanishes if f is a polynomial of degree $2M-1$ or less. The M quadrature points ξ_i and weights w_i can be determined whenever the first $2M$ moments μ_k ($k = 0, 1, 2, ..., 2M-1$) are known, and for this purpose a practical computational algorithm has been described (Gordon 1968 a). In several interesting cases the

sign of the remainder R is known, and the sum

$$\sum_{i=1}^{M} w_i f(\xi_i)$$

furnishes then a rigorous upper or lower bound to the true value of I.

Particularly for the distribution of *oscillator strengths*, Gordon has given lower bounds to the polarizability α by noting that the sum rules $S(k)$ furnish the required moments μ_k for the application of his technique. Since the zero-frequency polarizability α ($\omega = 0$) is, in atomic units, just the sum rule $S(-2)$, and since both Gordon's bounds and our formulae of § 3 provide the *best possible* lower bound for this quantity for the amount of information employed, it is clear that these two (seemingly dissimilar) approaches must actually give the *same* result when they use values of the same sum rules $S(k)$, as a simple calculation confirms.

In other applications the two bounding techniques may give complementary information. For example, the formulae of § 3 can furnish bounds for intermediate $S(k)$ in terms of those of both higher and lower k values, whereas Gordon's formulae require an uninterrupted sequence of these moments. On the other hand, our approach does not give bounds on, for example, the frequency-dependent polarizability, as Gordon was able to obtain.

5. Numerical illustrations

We shall illustrate the bounds of § 3 by some simple applications to small systems for which accurate values of the sum rules are known.

For the hydrogen atom the oscillator strength sum rules have been evaluated explicitly by Dalgarno and Kingston (1960). Choosing, for example, the polarizability sum rule $S(-2) = \alpha$, and using only 2×2 arrays of the sum rules $S(2)$–$S(-6)$ (except, of course, $S(-2)$ itself) we obtain

$$\alpha = 4 \cdot 49 \pm 0 \cdot 15 \, a_0{}^3$$

which may be compared with the exact answer $\alpha = 4 \cdot 5 \, a_0{}^3$. Using 3×3 arrays we obtain the results given in table 1 (notice that (*a*) is identical with Gordon's result), and from (*k*) and (*l*) we conclude

$$\alpha = 4 \cdot 498 \pm 0 \cdot 010 \, a_0{}^3.$$

If we go to 4×4 arrays we obtain the still stronger result

$$\alpha = 4 \cdot 5005 \pm 0 \cdot 0016 \, a_0{}^3$$

and, still using only the sum rules $S(2)$–$S(-6)$, we could improve this result even further by using a 5×5 Gramian and solving the resulting quintic equation. However, the examples given above may be sufficient to indicate the accuracy of which the method is capable.

For the negative hydrogen ion H⁻, values of $S(k)$ for $2 \geqslant k \geqslant -3$ may be obtained from the calculations of Pekeris (1962) and the compilation of Dalgarno and Ewart (1962)†. Using $S(2)$–$S(-1)$ in (3.1) we obtain the lower bound

$$\alpha \geqslant 124 \, a_0{}^3$$

which is already sufficient to rule out the values 91 or 101 calculated by the Sternheimer procedure (see Dalgarno 1962). Including $S(-3)$ and using (3.2) we obtain

$$\alpha \leqslant 229 \, a_0{}^3$$

which may be compared with the value $\alpha = 212 \pm 8$ quoted by Dalgarno and Ewart. Finally we may use a 4×4 Gramian to give a lower bound for the (unknown) value of $S(-4)$:

$$S(-4) \geqslant 8 \cdot 13 \times 10^4 \, \text{A.U.}$$

though this is to some extent subject to the uncertainties in the other sum rules.

† The values of $S(2)$ and $S(1)$ given by Dalgarno and Ewart appear to be in error. The actual values used here are as follows (all in A.U.): $S(2) = 1 \cdot 379$, $S(1) = 0 \cdot 7475$, $S(0) = 2$, $S(-1) = 14 \cdot 969$, $S(-2) = 212$, $S(-3) = 4000$.

Table 1. Upper and lower bounds for the oscillator strength sum rule $S(-2)$, the dipole polarizability, in the hydrogen atom ground state, as calculated from the formulae of § 3

	Formula	i	j	k	Lower bound	Upper bound
(a)	3·1	-1	0	1	4·125	—
(b)	3·1	-1	0	-3	4·456	—
(c)	3·1	-1	1	-2	4·378	—
(d)	3·1	-1	-2	-3	4·485	—
(e)	3·2	0	-2	-3	3·841	4·546
(f)	3·2	1	-3	0	0·072	14·261
(g)	3·2	-2	0	1	$(-2·965)$	4·965
(h)	3·2	-3	1	-2	3·353	6·755
(i)	3·2	$\frac{1}{2}$	$-\frac{5}{2}$	$-\frac{1}{2}$	4·124	6·626
(j)	3·2	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	1·459	4·541
(k)	3·2	$-\frac{3}{2}$	$-\frac{1}{2}$	$-\frac{5}{2}$	4·001	4·508
(l)	3·3	0	-1	-2	4·487	5·137
(m)	3·3	1	-1	-3	4·204	14·314

6. Improving the sum rule bounds

It is clear that the most effective way of improving our sum rule bounds is to have values of as many of the $S(k)$ as possible, particularly for values of k distributed around the value to be bounded. However, for practical purposes it is even more important that partial information about *individual* oscillator strengths can be brought to bear in improving the calculated bounds.

Suppose then that oscillator strengths f_{0n} and the associated excitation frequencies $E_n - E_0$ are known, either from experiment or from careful calculations, for the $p-1$ lowest-lying excited states of the system. Then for each k the contribution $S'(k)$ from this set of states to the sum rule $S(k)$ may be evaluated explicitly:

$$S'(k) = \sum_{n=1}^{p-1} f_{0n}(E_n - E_0)^k$$

while for the residual sum rule $S''(k) \equiv S(k) - S'(k)$ we may write in place of (2.3)

$$S''(k) = \int_{\omega_p}^{\infty} \omega^k \phi(\omega) \, d\omega \tag{6.1}$$

and proceed as before to place upper and lower bounds on the residues $S''(k)$.

Indeed, in place of (2.3) or (6.1) we might take, for example, the still more general form

$$S''(k) = \int_{\omega_1}^{\omega_p} \omega^k \phi(\omega) \, d\omega + \int_{\omega_q}^{\infty} \omega^k \phi(\omega) \, d\omega$$

where the interval between ω_p and ω_q may contain one or more bound states or even a band of the continuum for which the contribution to the sum rule has been evaluated explicitly. All the results of § 3 apply intact to these residual sum rules, and one may expect the bounds obtained in this fashion to be an important practical improvement. In a similar manner one may extend these bounds to *excited state* sum rules if oscillator strengths to all the lower-lying states have been evaluated.

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