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Bounds on mean excitation energies in terms of oscillator-strength moments

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The logarithmic mean excitation energies that determine, for fast charged particles, the total inelastic-scattering cross section, the stopping power, and the straggling are bounded *from above and below* by simple expressions involving moments of the oscillator-strength distribution. A general condition under which the set of elementary inequalities gives tight bounds is indicated, and is illustrated in several examples. Effective oscillator-strength distributions that are constructed on the basis of variational principles lead to tighter bounds in terms of some of the moments and the oscillator strengths for some discrete excitations.

I. INTRODUCTION

We consider the oscillator-strength density df/dE of an atom or a molecule in the ground state. This density is a function of the excitation energy E measured from the ground-state energy. The moment of the μth order is defined by

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

and its derivative with respect to the order μ is

$$L(\mu)=\frac{dS(\mu)}{d\mu} = \int \frac{df}{dE} E^{\mu} \ln E \, dE \ . \tag{2}$$

The integrals are taken over all continua and include the summation over discrete spectra. The mean excitation energies $I(\mu)$, defined by

$$\ln I(\mu)=L(\mu)/S(\mu) \ , \tag{3}$$

are crucial to many properties of the atom or molecule[1-5]; $I(-1)$ appears in the expression for the total inelastic-scattering cross section,[5] $I(0)$ in the Bethe formula for stopping power,[2] $I(1)$ in the Fano formula for straggling,[2] and $I(2)$ in the expression for the Lamb shift of energy levels.[1]

A fundamental electronic property of an atom or molecule, the oscillator-strength density, characterizes the response of matter to an electric field uniform in space and harmonic in time (at frequency $E/\hbar$). The study of df/dE in all aspects is important from both basic and applied standpoints. In particular, it is highly desirable to exploit relations among the indices of the distribution such as $S(\mu)$ and $L(\mu)$ and to obtain estimates of their values efficiently and reliably. The present work was motivated to contribute to this end.

Precise calculation of $L(\mu)$ is straightforward, if df/dE is completely known over the entire spectrum. Alternatively, one can derive $L(\mu)$ from the frequency-dependent polarizability, or more fundamentally, from the Green's function.[6,7] Either way, the calculation assumes full knowledge of the electronic structure, which is seldom available. $L(\mu)$ may be approximately calculated on the basis of variational principles.[6,8-13] This approach is equivalent to approximate determination of the Green's function, and involves cumbersome computations, when accurate results for many-electron systems are aimed at.

In contrast, $S(\mu)$ for $\mu=2,1,0,-1,-2,-4,-6,\ldots$ are either calculable as ground-state expectation values[1-4] or deducible from experiment.[2] Therefore, it is useful to establish means of estimating $L(\mu)$ from $S(\mu)$ without recourse to the full knowledge of df/dE or the Green's function. An example is to regard given $S(\mu)$ data as defining a function of a continuous variable μ, and then to deduce $L(\mu)$, either analytically[14-18] or graphically,[5] as the slope of the $S(\mu)$ curve. Another class of approaches is to use linear programming[19] or the moment theory,[20] i.e., general methods for inferring properties of the distribution from its moments.

The purpose of the present paper is twofold. First, we shall discuss in Sec. II a set of elementary upper and lower bounds on $\ln I(\mu)$ involving only oscillator-strength moments. Although the bounds themselves have been pointed out earlier,[19] our interpretation is new and leads to a criterion for judging their usefulness. Second, we shall derive, from variational principles, a series of tighter complementary bounds that are calculable from $S(\mu)$ and the oscillator strengths f_n for a finite number of discrete excitations. The elementary bounds in Sec. II will turn out to be the

simplest of these complementary bounds. Some of these complementary bounds also turn out to be identical with the moment-theory bounds of Ref. 20.

II. ELEMENTARY INEQUALITIES

A straightforward generalization of relation (5) of Ref. 19 gives inequalities

$$\ln[S(\mu)/S(\mu-1)] \leq L(\mu)/S(\mu) \leq \ln[S(\mu+1)/S(\mu)], \quad (4)$$

if all the quantities that appear here are well defined; $S(\mu)$ diverges in general at $\mu=\frac{5}{2}$ because of the asymptotic expression[1,3] $df/dE \propto E^{-7/2}$. The equality occurs only if df/dE degenerates into a single-line spectrum $S(0)\delta(E-E^*)$, E^* being a constant.

Mathematically, relation (4) is a consequence of Jensen's theorem about convex functions. One sets $\phi(z)=-\ln z$ and $\phi(z)=z\ln z$ in Eq. (6.14.1) of Ref. 21, and obtains relation (4) above.

The following alternative proof is more instructive. Assume that a function

$$T(\mu)=\ln S(\mu) \quad (5)$$

is twice differentiable. If the differentiation with respect to μ is denoted by a prime, one may write

$$T''(\mu)=\{S(\mu)S''(\mu)-[S'(\mu)]^2\}/[S(\mu)]^2 . \quad (6)$$

Note Eq. (2) and that

$$S''(\mu)=L'(\mu)=\int \frac{df}{dE} E^{\mu}(\ln E)^2 dE . \quad (7)$$

According to the Schwarz inequality, $T''(\mu)\geq 0$ for any μ, and the equality occurs only if $df/dE = S(0)\delta(E-E^*)$. In other words, $T(\mu)$ is convex downwards. Then, the slope $T'(\mu)=L(\mu)/S(\mu)$ at any μ is bounded from above and below by the slopes of two chords passing the point $(\mu, T(\mu))$, namely, by $[T(\mu+\nu)-T(\mu)]/\nu$ and $[T(\mu)-T(\mu-\nu')]/\nu'$, where ν and ν' are any real numbers for which $T(\mu+\nu)$ and $T(\mu-\nu')$ are well defined. Set $\nu=\nu'=1$, and relation (4) follows.

The essence of the proof is illustrated in Fig. 1, prepared from the data of Zeiss *et al.*,[22] and in Fig. 2, taken from the paper by Dehmer, Inokuti, and Saxon,[23] who extensively studied $S(\mu)$ for atoms. Cummings[24] also gave a similar figure. Indeed, $T(\mu)$ is convex downwards for all the relevant data on atoms (as quoted in Ref. 23) and on molecules (as quoted in Ref. 25), apart from one exception to be noted later. Evidently, relation (4) should give a set of tight bounds on $L(\mu)$ if $T''(\mu)$ is small, i.e., if the $T(\mu)$ curve is nearly linear. Therefore, Fig. 2 immediately shows

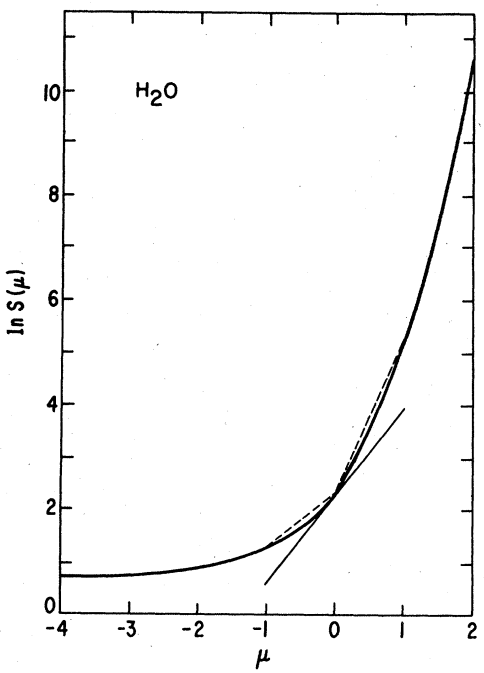

FIG. 1. Illustration of inequalities (4) for the H_2O molecule. All data are due to Zeiss *et al.*[22] The thin straight line is the tangent of the $\ln S(\mu)$ curve at $\mu=0$. The broken straight lines (- - -) are chords passing the point (0,1). Clearly, the slopes of the chords bound the slope of the tangent from above and below.

that the bounds on $L(-1)/S(-1)$ of He are quite tight, and those on $L(0)/S(0)$ of He fairly tight. For Ne, the bounds on $L(-1)/S(-1)$ and $L(0)/S(0)$ are looser than those for He. For Li, the lower

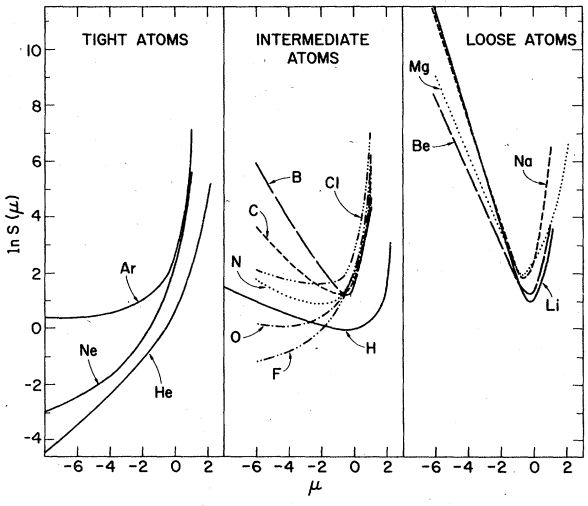

FIG. 2. $\ln S(\mu)$ of lighter atoms plotted as a function of μ. The curve for H is rigorous. The curves for He, Ne, and Ar are based on the best data available. All the other curves are based on the calculation[23] in the Hartree-Slater model.

bound on $L(-1)/S(-1)$ is tight, but the upper bound is looser. In general, bounds on $L(1)/S(1)$ are much looser, because $T''(1)$ is appreciable; recall that $S(\mu)$, $L(\mu)$, and $T(\mu)$ are all divergent at $\mu = 2.5$.[1,3]

Table I illustrates bounds for $\mu = -1$, 0, 1, and 2 obtained from data[3,5,8,9,25,26] for H, He, Ne, and H_2O, and corroborates all the observations in the previous paragraph.

An additional commentary concerns three points. First, relation (4) holds whatever energy unit is used for $S(\mu)$ and $L(\mu)$, but each term in relation (4) has a value dependent on the energy unit. The scale change by a factor α causes each term to increase by a common additive constant $\ln\alpha$. Then, $T(\mu)$ increases by an additive term $\mu\ln\alpha$, but $T''(\mu)$ remains invariant. Thus, in Table I, it is the difference (which is independent of the energy scale) between two successive entries that represents the tightness of the bounds.

Second, relation (4) holds also for partial contributions to $S(\mu)$ and $L(\mu)$ either from a limited spectral region or from specified shells or subshells to the extent that shell or subshell contributions are well defined. As an application, divide $S(\mu)$ and $L(\mu)$ into two partial contributions, so that $S(\mu) = S_<(\mu) + S_>(\mu)$ and $L(\mu) = L_<(\mu) + L_>(\mu)$. Suppose that $S_<(\mu)$ and $L_<(\mu)$ are known in addition to $S(\mu)$. Then, applying (4) to $L_>(\mu)$ and $S_>(\mu)$, one obtains bounds on $L_>(\mu)/S_>(\mu)$, and therefore on $L(\mu)/S(\mu)$:

$$\frac{S_>(\mu)}{S(\mu)}\left[\frac{L_<(\mu)}{S_>(\mu)} + \ln\left(\frac{S_>(\mu)}{S_>(\mu-1)}\right)\right] \leq \frac{L(\mu)}{S(\mu)} \leq \frac{S_>(\mu)}{S(\mu)}\left[\frac{L_<(\mu)}{S_>(\mu)} + \ln\left(\frac{S_>(\mu+1)}{S_>(\mu)}\right)\right]. \tag{8}$$

We recommend that $\ln S(\mu)$ be plotted against μ each time data on any atom or molecule become available and that the downward convexity of the resulting curve be verified. To illustrate the usefulness of the recommendation, we may quote the work of Turner *et al.*[27] Figure 1 of Ref. 27 presents $S(\mu)$ data for H, Al, and U atoms. (The index r of Ref. 27 corresponds to our $\mu + 1$.) Against our rule the curves for Al and U show upward convexity. Examination of the numerical work reveals that the values of $S(1)$ (shown at $r = 2$ in the figure) for Al and U are too large by a factor of Z. Correction of the error renders all the curves convex downwards and resolves the difficulty.

TABLE I. Test of inequalities (4). $S(\mu)$ and $L(\mu)$ are defined by Eqs. (1) and (2) with excitation energies E measured in units of the Rydberg energy (13.606 eV). Entries for each column increase steadily from top to bottom according to the inequalities. Numerical values are based on data in Refs. 3, 5, 7, 8, 25, and 26.

Terms in Eq. (4)	H	He	Ne	H_2O
$\ln[S(-1)/S(-2)]$	−0.1178	0.777	1.04	0.426
$L(-1)/S(-1)$	−0.0733	0.848	1.25	0.607
$\ln[S(0)/S(-1)]$	0.0000	0.978	1.67	0.997
$L(0)/S(0)$	0.0970	1.13	2.31	1.65
$\ln[S(1)/S(0)]$	0.2877	1.41	3.46	2.95
$L(1)/S(1)$	0.5709	1.68	4.65	4.23
$\ln[S(2)/S(1)]$	1.3863	2.70	5.79	5.41
$L(2)/S(2)$	2.9841	4.37	7.19	7.19

III. IMPROVED BOUNDS IN TERMS OF OSCILLATOR-STRENGTH MOMENTS

In this section we shall first consider a set of basis functions $\{u_i\}$, in terms of which we shall define two finite subspaces of the Hilbert space of square-integrable functions. Projections of the Schrödinger equation onto these subspaces will be considered, and two sets of effective discrete excited states will be defined. Using these sets, we shall construct two types of *an effective discrete oscillator-strength distribution*. These effective spectra play an important role in this section. If a certain function, defined later, is included in the basis set $\{u_i\}$, the effective spectra reproduce exactly some of the oscillator-strength moments $S(\mu)$, but not $L(\mu)$. They give, however, upper and lower bounds on some of the $L(\mu)$. (These bounds prove to be the optimum values given by complementary variational principles, as will be seen in Sec. IV.)

Choosing a special basis set, we shall derive simple bounds on $L(\mu)$ in terms of data available for many atoms, namely, moments of the entire oscillator-strength distribution and the positions E_{0n} and the oscillator strengths f_n of some discrete spectral lines. We shall illustrate on some atoms the usefulness of these simple bounds for $\mu = -1$, 0, and 1; results for $\mu = 2$ are somewhat discouraging. The simplest examples of the bounds in terms of $S(\mu)$ are identical with those derived in the preceding section from the downward convexity of the curve of $\ln S(\mu)$ vs μ.

A. Effective oscillator-strength distributions

In the following we use the Rydberg unit for energy and atomic units for other quantities. Consider eigenvalues E_n and normalized eigenfunctions ψ_n of the Hamiltonian H of an atom. Let ψ_0 be the ground state and ψ_n with $n \geq 1$ be the excited states that are coupled with ψ_0 by the dipole operator $D = \Sigma_{zi}$. We assume that the atom is either spherical or randomly oriented. In terms of a function $\varphi^{(s)}$ defined by

$$\varphi^{(s)} = (H - E_0)^{s/2} D \psi_0 , \tag{9}$$

the oscillator strength for the transition $\psi_0 \to \psi_n$ may be written as

$$f_n = E_{0n}^{1-s} |(\psi_n, \varphi^{(s)})|^2 , \tag{10}$$

where $E_{0n} = E_n - E_0$ is the excitation energy. The choices $s = 0$ and 2 give length-form and velocity-form expressions; recall that

$$(H - E_0) D \psi_0 = -2 \sum \frac{\partial}{\partial z_i} \psi_0 .$$

For a real atom there are infinitely many discrete states ψ_n and a continuum of excited states that are accessible from the ground state by a dipole-allowed transition. For constructing an effective oscillator-strength distribution, the Hilbert space $\mathfrak{X}_d$ of these functions may be approximated by a finite subspace $\mathfrak{X}_d^1$ spanned by basis functions $\{u_i\}_{i=1}^N$; some choices of $\{u_i\}$ will be discussed later. Assume that the ground-state energy E_0 is known, and define matrices $\underline{A}$ and $\underline{B}$ by

$$A_{ij} = (u_i | H - E_0 | u_j) \tag{11a}$$

and

$$B_{ij} = (u_i, u_j) . \tag{11b}$$

Matrix $\underline{B}$ is symmetric and positive definite. So is $\underline{A}$, because the basis functions u_i belong to $\mathfrak{X}_d$. Consider a matrix eigenvalue problem

$$\underline{A} \underline{c}_n = \varepsilon_n \underline{B} \underline{c}_n , \tag{12}$$

which is the Schrödinger equation projected onto $\mathfrak{X}_d^1$. An orthonormality relation

$$\underline{c}_n^T \underline{B} \underline{c}_m = \delta_{nm} \tag{13}$$

holds, if the normalization constants are chosen appropriately. Here, the superscript T indicates a transposed row vector, and $\underline{c}_n$ is a column vector having components $(c_n)_i$. An orthonormal set of approximate excited states are obtained as

$$\phi_n = \underline{c}_n^T \cdot \underline{u} = \sum_{i=1}^N (c_n)_i u_i \quad (n = 1, \cdots, N) . \tag{14}$$

The eigenvalues ε_n of Eq. (12) are the excitation energies corresponding to ϕ_n and measured from the ground-state energy E_0.

Choose $u_1 = \varphi^{(s)}$. Then, $A_{11} = S(s)$, because

$$S(\mu) = (\psi_0 | D[H - E_0]^{\mu+1} D | \psi_0) . \tag{15}$$

Therefore, A_{11} for $s \geq \frac{5}{2}$ are infinite, and we consider only $s < \frac{5}{2}$. An effective oscillator-strength distribution may be defined by the set of the excitation energies ε_n and effective oscillator strengths

$$f_n^{(s)} = \varepsilon_n^{1-s} |(\phi_n, \varphi^{(s)})|^2 \tag{16a}$$

$$= \varepsilon_n^{1-s} [\underline{B} \underline{c}_n \underline{c}_n^T \underline{B}]_{11} \tag{16b}$$

for $n = 1, \cdots, N$; compare Eq. (16a) with Eq. (10). In using $\varphi^{(s)}$ in the definition of $f_n^{(s)}$, we have assumed knowledge of the exact ψ_0. The effective spectrum $\{\varepsilon_n, f_n^{(s)}\}$ differs from the true spectrum, having only a discrete spectrum and being confined in a finite region of energy. Nevertheless, it shares some of the overall properties with the true spectrum. The moment of the effective spectrum $\{\varepsilon_n, f_n^{(s)}\}$ and its derivative with respect to the order μ are

$$S^{(s)}(\mu) = \sum_{n=1}^N f_n^{(s)} \varepsilon_n^\mu \tag{17a}$$

and

$$L^{(s)}(\mu) = \sum_{n=1}^N f_n^{(s)} \varepsilon_n^\mu \ln \varepsilon_n . \tag{17b}$$

Appendix A shows that, because of the inclusion of the exact $\varphi^{(s)}$ in the basis set $\{u_i\}$, the moments $S^{(s)}(s-1)$ and $S^{(s)}(s)$ are exact, i.e.,

$$\left.\begin{aligned} S^{(s)}(s-1) &= S(s-1) , \\ S^{(s)}(s) &= S(s) \end{aligned}\right\} \quad \text{for } s < \tfrac{5}{2} . \tag{18}$$

We shall show in Sec. IV that $L^{(s)}(s-1)$ and $L^{(s)}(s)$ are variationally optimized bounds on $L(s-1)$ and $L(s)$:

$$\left.\begin{aligned} L^{(s)}(s-1) &\geq L(s-1) , \\ L^{(s)}(s) &\leq L(s) \end{aligned}\right\} \quad \text{for } s < \tfrac{5}{2} . \tag{19}$$

Combination of Eqs. (18) and (19) gives bounds on mean excitation energies. So far the basis functions u_i except u_1 have not been specified. By so choosing u_i that $L^{(s)}(s-1)$ becomes as small as possible and $L^{(s)}(s)$ as large as possible, one may obtain good estimates of $\ln I(s-1)$ and $\ln I(s)$.

If the basis set includes both $\varphi^{(0)}$ and $\varphi^{(2)}$, it follows, in addition to Eqs. (18) and (19), that

$$S^{(0)}(1) = S(1), \quad S^{(0)}(2) = S(2) \tag{20}$$

and

$$L^{(0)}(1) \geq L(1), \quad L^{(0)}(2) \leq L(2) . \tag{21}$$

Next, we construct another effective oscillator-strength distribution. We assume knowledge of

both the ground-state energy E_0 and the energy E_1 of the lowest excited state ψ_1 belonging to $\mathfrak{X}_d$. Instead of $\{u_i\}_{i=1}^N$, we consider a basis set $\{(H-E_1)^{1/2}u_i\}_{i=1}^N$. Then, the Schrödinger equation projected onto the functional space $\mathfrak{X}_d^2$ spanned by this set of functions is

$$\underline{V}\underline{d}_n=\epsilon_n\underline{W}\underline{d}_n \quad (n=2,3,\cdots,N+1), \tag{22}$$

where the matrices $\underline{V}$ and $\underline{W}$ are defined by

$$V_{ij}=(u_i|[H-E_0][H-E_1]|u_j)$$
$$=X_{ij}-E_{01}A_{ij}, \tag{23a}$$

$$W_{ij}=(u_i|H-E_1|u_j)=A_{ij}-E_{01}B_{ij}, \tag{23b}$$

and

$$X_{ij}=(u_i|[H-E_0]^2|u_j). \tag{23c}$$

Because of the operator $(H-E_1)$, a ψ_1 component in u_i contributes nothing. Therefore, we choose functions u_i so that ψ_1 does not belong to $\mathfrak{X}_d^1$. Then, both $\underline{V}$ and $\underline{W}$ are symmetric and positive definite. On the other hand, an effective spectrum should include a contribution from ψ_1, which will be considered later. This is the reason why in Eq. (22) the eigenvalues are numbered from 2 to $N+1$ instead of 1 to N. Due to the orthonormality relation

$$\underline{d}_n^T\underline{W}\underline{d}_m=\delta_{nm}, \tag{24}$$

we obtain an orthonormal set of approximate excited states

$$\phi_n=\underline{d}_n^T(H-E_1)^{1/2}\underline{u} \quad (n=2,\ldots,N+1) \tag{25}$$

having excitation energies ϵ_n measured from the ground-state energy E_0. Naturally, we should take $\phi_1=\psi_1$ and $\epsilon_1=E_{01}$.

Choose $u_1=\varphi^{(s)}$. Then, because of Eq. (15), $X_{11}=S(s+1)$, which is infinite for $s\geq\frac{3}{2}$; we consider only $s<\frac{3}{2}$. The oscillator strength in Eq. (10) may be written in a different form

$$f_n=E_{0n}^{1-s}\left|(\psi_n|[H-E_1]^{1/2}|\varphi^{(s)})\right|^2/(E_{0n}-E_{01}), \tag{26}$$

the denominator being the excitation energy measured from the lowest excited state ψ_1. Effective oscillator strengths may be defined as

$$g_n^{(s)}=\epsilon_n^{1-s}\left|(\phi_n|[H-E_1]^{1/2}|\varphi^{(s)})\right|^2/(\epsilon_n-\epsilon_1) \tag{27a}$$

$$=\epsilon_n^{1-s}(\underline{W}\underline{d}_n\underline{d}_n^T\underline{W})_{11}/(\epsilon_n-\epsilon_1) \tag{27b}$$

for $n=2,\ldots,N+1$. For $n=1$, Eq. (27a) has a zero-over-zero form, and $g_1^{(s)}$ is determined so as to satisfy

$$\sum_{n=1}^{N+1}g_n^{(s)}\epsilon_n^{s-1}=S(s-1). \tag{28}$$

The moment of this effective spectrum and its derivative are

$$\mathcal{S}^{(s)}(\mu)=\sum_{n=1}^{N+1}g_n^{(s)}\epsilon_n^{\mu} \tag{29a}$$

and

$$\mathcal{L}^{(s)}(\mu)=\sum_{n=1}^{N+1}g_n^{(s)}\epsilon_n^{\mu}\ln\epsilon_n. \tag{29b}$$

According to Eq. (28) and Appendix A,

$$\mathcal{S}^{(s)}(s-1)=S(s-1),$$
$$\mathcal{S}^{(s)}(s)=S(s), \tag{30}$$

and

$$\mathcal{S}^{(s)}(s+1)=S(s+1)$$

for $s<\frac{3}{2}$. We shall show in Sec. IV that some of the $\mathcal{L}^{(s)}(\mu)$ are variational bounds on $L(\mu)$:

$$\mathcal{L}^{(s)}(s-1)\leq L(s-1),$$
$$\mathcal{L}^{(s)}(s)\geq L(s), \tag{31}$$

and

$$\mathcal{L}^{(s)}(s+1)\leq L(s+1)$$

for $s<\frac{3}{2}$. For a fixed s, these inequalities give bounds complementary to those obtained from the effective spectrum $\{\varepsilon_n,f_n^{(s)}\}_{n=1}^N$. However, no upper bound on $L(\mu)$ has been obtained for $\frac{3}{2}\leq\mu<\frac{5}{2}$.

B. Examples of simple bounds

In this section we shall assume a special type of basis functions for constructing effective oscillator-strength spectra. Then, all the elements of matrices $\underline{A}$, $\underline{B}$, $\underline{V}$, and $\underline{W}$ are expressible in terms of $S(\mu)$, and some discrete oscillator strengths f_n and the corresponding excitation energies E_{0n}. Thus, we can derive from the variational bounds on mean excitation energies, studied in Sec. III A, bounds in terms of these known quantities. A special case of a single-member basis set leads to a single-line effective spectrum that gives bounds equivalent to inequalities (4) in Sec. II. If this basis set is augmented by another kind of basis functions, we obtain inequalities (8). The bounds calculable from several $S(\mu)$ and (f_n,E_{0n}) will be tested on H, He, Ne, and H_2O. The bounds on $L(-1)$, $L(0)$, and $L(1)$ will prove to be useful.

Let the basis set $\{u_i\}$ be

$$u_i=\begin{cases}(H-E_0)^{m_i}\varphi^{(s)} & (1\leq i\leq N_0)\\ \psi_{n_i} & (N_0+1\leq i\leq N)\end{cases}. \tag{32}$$

Similar basis set has been used by Goscinski[28] in calculations of bounds on frequency-dependent polarizabilities. For the present purpose, m_1 for $i=1$ must be zero. For $i\geq 2$, m_i may be any

integer, insofar as all the elements of matrices A and B (for constructing the effective spectrum $\{\varepsilon_n, f_n^{(s)}\}$) or V and W (for $\{\epsilon_n, g_n^{(s)}\}$) are well defined. When inequalities (21) are used, $s=0$, and u_i with $m_i=1$ must be included. The wave functions ψ_{n_i} in Eq. (32) are those eigenfunctions of H which belong to $\mathfrak{X}_d$, and may be numbered in any order. For obtaining the effective spectrum $\{\epsilon_n, g_n^{(s)}\}$, ψ_1 must be excluded from the basis set, according to the statement made just below Eq. (23c).

The matrices $\underline{B}$, $\underline{A}$, and $\underline{X}$ may be decomposed into submatrices as

$$\underline{B}=\begin{pmatrix}\underline{B}_a & \underline{B}_b\\ \underline{B}_b^T & \underline{B}_c\end{pmatrix}, \tag{33}$$

etc., corresponding to the division of the basis functions into two groups $i\leq N_0$ and $i>N_0$. The matrix elements are obtained from Eqs. (9), (10), and (15) as

$$(B_a)_{ij}=S(s+m_i+m_j-1),\quad (B_b)_{ij}=f_{nj}^{1/2}E_{0nj}^{(s+2m_i-1)/2},\quad (B_c)_{ij}=\delta_{ij}, \tag{34a}$$

$$(A_a)_{ij}=S(s+m_i+m_j),\quad (A_b)_{ij}=f_{nj}^{1/2}E_{0nj}^{(s+2m_i+1)/2},\quad (A_c)_{ij}=E_{0n_i}\delta_{ij}, \tag{34b}$$

$$(X_a)_{ij}=S(s+m_i+m_j+1),\quad (X_b)_{ij}=f_{nj}^{1/2}E_{0nj}^{(s+2m_i+3)/2},\quad (X_c)_{ij}=E_{0n_i}^2\delta_{ij}. \tag{34c}$$

Here, we have assumed that all the wave functions ψ_{n_i} are real and normalized, and the signs of the normalization constants have been so chosen that $(\psi_0|D|\psi_{n_i})>0$. Matrices V and W are given by Eqs. (23a) and (23b). Note that all the matrices necessary for calculating bounds on $L(\mu)$ are obtained from data available for many atoms, namely, moments of the entire oscillator-strength distribution and the oscillator strengths and excitation energies for some discrete transitions.

The simplest basis set $\{u_i\}$ consists of a single member $u_1=\varphi^{(s)}$. Then, $\underline{B}$ and $\underline{A}$ are one-by-one matrices, and $B=S(s-1)$ and $A=S(s)$ [Eq. (A5) in Appendix A]. The corresponding effective spectrum is a single-line spectrum

$$\{\varepsilon_1=S(s)/S(s-1),\ f_1^{(s)}=[S(s-1)]^s[S(s)]^{1-s}\}.$$

Naturally, this spectrum satisfies Eq. (18); $f_1^{(s)}\varepsilon_1^{s-1}=S(s-1)$ and $f_1^{(s)}\varepsilon_1^{s}=S(s)$. From Eqs. (17b) and (19) we obtain inequalities

$$\frac{L(s-1)}{S(s-1)}\leq\frac{L^{(s)}(s-1)}{S(s-1)}=\ln\left(\frac{S(s)}{S(s-1)}\right)=\frac{L^{(s)}(s)}{S(s)}\leq\frac{L(s)}{S(s)}\quad\left(s<\tfrac{5}{2}\right), \tag{35}$$

which are equivalent to inequalities (4). Thus, the bounds derived in this section may be regarded as generalizations of inequalities (4).

If $N_0=1$ and $u_i=\psi_{ni}$ for $i=2,\ldots,N$, the matrices $\underline{B}$ and $\underline{A}$ are

$$\underline{B}=\begin{pmatrix}S(s-1) & \beta_2 & \beta_3 & \cdots & \beta_N\\ \beta_2 & 1 & 0 & \cdots & 0\\ \beta_3 & 0 & 1 & \cdots & 0\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ \beta_N & 0 & 0 & \cdots & 1\end{pmatrix}\quad(\beta_i=\{f_{n_i}E_{0n_i}^{s-1}\}^{1/2}), \tag{36a}$$

and

$$\underline{A}=\begin{pmatrix}S(s) & E_{0n_2}\beta_2 & E_{0n_3}\beta_3 & \cdots & E_{0n_N}\beta_N\\ E_{0n_2}\beta_2 & E_{0n_2} & 0 & \cdots & 0\\ E_{0n_3}\beta_3 & 0 & E_{0n_3} & \cdots & 0\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ E_{0n_N}\beta_N & 0 & 0 & \cdots & E_{0n_N}\end{pmatrix}. \tag{36b}$$

The eigenvalues and normalized eigenvectors of Eq. (12) are

$$\varepsilon_1 = F(s)/F(s-1), \qquad \varepsilon_i = E_{0n_i} \quad (i=2,\ldots,N) \tag{37a}$$

and

$$\underline{c}_1 = [F(s-1)]^{-1/2} \begin{bmatrix} 1 \\ -\beta_2 \\ -\beta_3 \\ \vdots \\ -\beta_N \end{bmatrix},$$

$$\underline{c}_i = \begin{bmatrix} 0 & 1 \\ \vdots & \vdots \\ 0 & i-1 \\ 1 & i \\ 0 & i+1 \\ \vdots & \vdots \\ 0 & N \end{bmatrix} \quad (i=2,\ldots,N), \tag{37b}$$

where

$$F(s) = S(s) - \sum_{i=2}^{N} f_{n_i} E_{0n_i}^s. \tag{37c}$$

It follows from Eq. (16b) that

$$f_1^{(s)} = [F(s-1)]^s [F(s)]^{1-s}$$

and (38)

$$f_i^{(s)} = f_{n_i} \quad (i=2,\ldots,N).$$

Therefore, in the N-line effective spectrum, the positions and the strengths of the $N-1$ input lines remain unchanged. The only remaining line $(\varepsilon_1, f_1^{(s)})$ has been determined, in effect, so as to reproduce $S(s-1)$ and $S(s)$ exactly. Bounds on $L(\mu)$ are obtained as

$$L(s) \leq L^{(s+1)}(s) = F(s)\left[\frac{L_<(s)}{F(s)} + \ln\left(\frac{F(s+1)}{F(s)}\right)\right] \quad (s<\tfrac{3}{2}) \tag{39a}$$

and

$$L(s) \geq L^{(s)}(s) = F(s)\left[\frac{L_<(s)}{F(s)} + \ln\left(\frac{F(s)}{F(s-1)}\right)\right] \quad (s<\tfrac{5}{2}), \tag{39b}$$

where

$$L_<(s) = \sum_{i=2}^{N} f_{n_i} E_{0n_i}^s \ln E_{0n_i}. \tag{39c}$$

Inequalities (39a) and (39b) are equivalent to inequalities (8), because $F(s)$ and $L_<(s)$ play the same roles as $S_>(\mu)$ and $L_<(\mu)$ in inequalities (8).

Because $S(\mu)$ values for several μ are available for many atoms, it is useful to illustrate on the hydrogen atom, for which the exact value of $S(\mu)$ is known for any μ, how the bounds in terms of $S(\mu)$ are improved as N_0 is increased, i.e., as more and more $S(\mu)$ are used as an input. Table II shows that the improvement is very rapid for $\mu=-1$ and 0, and fairly rapid for $\mu=1$, suggesting the usefulness of the bounds derived in this section. For $\mu=2$, however, only a lower bound can be obtained, and it converges slowly. Thus the method of this section may often be of little use for estimating $\ln I(2)$.

A straightforward generalization of Appendix A shows that the effective spectra of this section exactly reproduce the moments $S(\mu)$ that are used to construct these spectra. When discrete oscillator strengths f_n are not used, i.e., when $N=N_0$ in Eq. (32) an N-point spectrum $\{\varepsilon_n, f_n^{(s)}\}$ is, in effect, determined so that $2N$ moments be reproduced, and an $(N+1)$-point spectrum $\{\epsilon_n, g_n^{(s)}\}$ is, in effect, determined so that $2N+1$ moments and E_{01} be reproduced. In fact this procedure has been taken by Langhoff and Yates[20] for obtaining bounds on the basis of the moment theory. Their upper bounds on $L(0)$ and lower bounds on $L(1)$ and on $L(-1)$ are determined from $S(\mu)$ for $\mu=1,0,\ldots,2-2N$, and their lower bounds on $L(0)$ and upper bounds on $L(1)$ and on $L(-1)$ are determined from E_{01} and $S(\mu)$ for $\mu=2,1,\ldots,4-2N$. Thus, the moment-theory bounds of Ref. 20 are special cases of the complementary bounds of this section (cf. footnote c of Table II). Table 1 of Ref. 20 is indeed consistent with Table II of the present paper within round-off errors, except for the following: If the mean excitation energies are given in eV, our upper bound on $\ln I(1)$ in terms of $S(2) \sim S(-2)$ and E_{01} is 3.245 as compared with 3.241 in Ref. 20. In passing, Table 1 of Ref. 20 includes "upper and lower bounds" on $\ln I(-1)$ in terms of $S(2) \sim S(0)$ and E_{01}, but they are really not guaranteed to be bounds either by the arguments of the present paper or by the moment theory of Ref. 20.

Table III illustrates bounds obtained from data[3,5,8,14,25,26,29] for He, Ne, and H_2O, and proves the usefulness of the bounds for $\mu=-1$, 0, and 1. Naturally, the bounds are rigorous only if all the input data are exact, which is true only for atomic hydrogen. When two complementary bounds are close to each other, we should be careful of the accuracy of the input data, because either of the

TABLE II. Bounds on $L(\mu)$ for the hydrogen atom in the ground state that are obtained from oscillator-strength moments $S(\nu)$ and the first excitation energy E_{01}. Energies are measured in Rydberg units.

	$L(2)$	$L(1)$	$L(0)$	$L(-1)$
Input data	Lower bound	Upper bound	Lower bound	Upper bound
$S(2)\sim S(1)$	7.39	1.848	0.0000 [a]	0.000 00 [a]
$S(2)\sim S(0)$, E_{01}	9.52	1.104 [c]	−0.0874 [c]	
$S(2)\sim S(-1)$	10.61	0.933	0.0549	−0.025 75
$S(2)\sim S(-2)$, E_{01}	11.59	0.846 [c]	0.0857 [c]	−0.068 12 [c]
$S(2)\sim S(-3)$	12.03	0.820	0.0913	−0.071 58
$S(2)\sim S(-4)$, E_{01}	12.61	0.796 [c]	0.0948 [c]	−0.072 85 [c]
$S(2)\sim S(-5)$	12.85	0.788	0.0956	−0.073 05
Input data		Lower bound	Upper bound	Lower bound
$S(1)\sim S(0)$		0.384 [c]	0.2877 [c]	−0.117 78 [b]
$S(1)\sim S(-1)$, E_{01}		0.592	0.1305	−0.108 47
$S(1)\sim S(-2)$		0.654 [c]	0.1102 [c]	−0.079 84 [c]
$S(1)\sim S(-3)$, E_{01}		0.701	0.1015	−0.074 47
$S(1)\sim S(-4)$		0.716 [c]	0.0996 [c]	−0.073 77 [c]
$S(1)\sim S(-5)$, E_{01}		0.732	0.0981	−0.073 41
Exact value	15.92	0.761	0.0970	−0.073 25

[a] Input data: $S(0)$ and $S(-1)$.
[b] Input data: $S(-1)$ and $S(-2)$.
[c] Bounds obtainable also from the moment theory of Ref. 20.

bounds may cross over the true value owing to an error in the input.

IV. COMPLEMENTARY VARIATIONAL BOUNDS

The mean excitation energies may be expressed in terms of $S(\mu)$ and a kind of frequency-dependent Green's function $G^{(s)}(\omega)$ that depends on the function $\varphi^{(s)}$. We shall derive complementary variational bounds on $G^{(s)}(\omega)$, and hence, on $L(\mu)$. The optimum bounds may be expressed in terms of the effective spectra defined in Sec. III. The results have the same form as the definition of

TABLE III. Bounds on mean excitation energies $I(\mu)$ in terms of discrete oscillator strengths f_n and oscillator-strength moments $S(\nu)$. Energies are measured in Rydberg units. These values should be compared with $\ln I(\mu)=L(\mu)/S(\mu)$ in Table I.

		He	Ne	H_2O
$\ln I(-1)$	Upper bound	0.857 (0.87) [a]	1.28 (1.38)	0.64
	Lower bound	0.855 (0.85)	1.24 (1.16)	0.58
	Difference	0.002 (0.02)	0.04 (0.22)	0.05
$\ln I(0)$	Upper bound	1.135 (1.16)	2.39 (2.51)	1.77
	Lower bound	1.127 (1.10)	2.18 (1.99)	1.50
	Difference	0.008 (0.06)	0.21 (0.52)	0.27
$\ln I(1)$	Upper bound	1.841 (1.90)	5.08 (5.31)	4.76
	Lower bound	1.755 (1.66)	4.25 (4.03)	3.75
	Difference	0.086 (0.24)	0.83 (1.28)	1.01
$\ln I(2)$	Lower bound	3.568	6.06	5.64
	Input data	$S(2)\sim S(-4)$ (f_1, E_{01}) (f_2, E_{02})	$S(2)\sim S(-4)$ (f_1, E_{01}) (f_2, E_{02})	$S(2)\sim S(-4)$ E_{01}

[a] Values in parentheses are from Ref. 20.

the exact $L(\mu)$, except that the integration over the continuous spectra in the exact $L(\mu)$ is absent in the expressions for the bounds, and is replaced by the summation over the discrete effective spectra. Thus, inequalities (19), (21), and (31) will be proved on the basis of variational principles.

Shimamura and Watanabe[13] have obtained variational bounds on $L(\mu)$ for $\mu=-1$, 0, 1, and 2, which include as special cases bounds obtained by other authors, namely, bounds on $L(2)$ by Schwartz[8] and by Dmitriev *et al.*,[10,11] on $L(0)$ and $L(1)$ by Chan and Dalgarno[6] and by Kamikawai *et al.*,[9] and on $L(-1)$ and $L(0)$ by Yuriev.[12] The following formulation is a generalization of that of Ref. 13.

We begin with two functionals $J[\chi]$ and $I[\chi]$ of a real function χ that have been discussed by Shimamura[30] (See also Ref. 31.):

$$J[\chi]=(\chi, 2u-\mathcal{A}\chi) \tag{40a}$$

$$I[\chi]=(u-\mathcal{A}\chi, u-\mathcal{A}\chi)/\lambda_0+J[\chi]. \tag{40b}$$

Here, u is a real function, $\mathcal{A}$ is a linear and positive-definite operator, and λ_0 is the smallest eigenvalue of $\mathcal{A}$. These functionals are variational and bound from above and below the expectation value of the inverse of $\mathcal{A}$ with respect to u, i.e.,

$$J[\chi_1]\le(u\,|\,\mathcal{A}^{-1}\,|\,u)\le I[\chi_2] \tag{41}$$

for any real χ_1 and χ_2.[30] The first equality holds if

$$\mathcal{A}\chi_1-u=0, \tag{42a}$$

and the second holds if

$$(\mathcal{A}-\lambda_0)(\mathcal{A}\chi_2-u)=0. \tag{42b}$$

Inequalities (41) give tight bounds, if the trial functions χ_1 and χ_2 satisfy Eqs. (42a) and (42b) to a good approximation.

Set

$$\mathcal{A}=H-E_0+\omega \quad\text{and}\quad u=u_1=\varphi^{(s)}, \tag{43}$$

where ω is any positive constant. Let χ_1 and χ_2 belong to $\mathfrak{X}_d$. Naturally, $\mathcal{A}>0$ and $\lambda_0=E_{01}+\omega>0$. Then, inequalities (41) give bounds on the quantity

$$G^{(s)}(\omega)=(\varphi^{(s)}\,|\,[H-E_0+\omega]^{-1}\,|\,\varphi^{(s)})$$

$$=\sum_n f_n\left(\frac{E_{0n}^{s-1}}{E_{0n}+\omega}\right)\quad(s<\tfrac{5}{2}), \tag{44}$$

and Eq. (42a) is the first-order perturbation equation for frequency (ω)-dependent dipole perturbation. The solution of Eq. (42a) satisfies also Eq. (42b).

Assume trial functions of the form

$$\chi_{1,2}(\omega)=\sum_{i=1}^{N} c_i(\omega)u_i=\underline{c}^T\underline{u}. \tag{45}$$

Then, the variational functionals that bound $G^{(s)}(\omega)$ take forms quadratic in $\underline{c}$ as

$$J[\chi_1]=2(\underline{c}^T\underline{B})_1-\underline{c}^T(\underline{A}+\omega\underline{B})\underline{c} \tag{46a}$$

and

$$I[\chi_2]=(E_{01}+\omega)^{-1}[B_{11}-2(\underline{c}^T\underline{W})_1+\underline{c}^T(\underline{V}+\omega\underline{W})\underline{c}], \tag{46b}$$

the matrices $\underline{A}$, $\underline{B}$, $\underline{V}$, and $\underline{W}$ being defined by Eqs. (11) and (23). The optimum values of Eqs. (46a) and (46b) are

$$J_{\max}(\omega)=[\underline{B}(\underline{A}+\omega\underline{B})^{-1}\underline{B}]_{11} \tag{47a}$$

and

$$I_{\min}(\omega)=(E_{01}+\omega)^{-1}[\underline{B}-\underline{W}(\underline{V}+\omega\underline{W})^{-1}\underline{W}]_{11}, \tag{47b}$$

because both $\underline{A}+\omega\underline{B}$ and $\underline{V}+\omega\underline{W}$ are positive definite. [See the statements made just below Eq. (11) and Eq. (23).] Using Eq. (16b) and Eqs. (A1) and (A2) in Appendix A, one may show that

$$J_{\max}(\omega)=\sum_{n=1}^{N} f_n^{(s)}\left(\frac{\varepsilon_n^{s-1}}{\varepsilon_n+\omega}\right). \tag{48a}$$

Similarly, from Eqs. (27b), (A3), (A6), and (A7),

$$I_{\min}(\omega)=(\epsilon_1+\omega)^{-1}\left[S^{(s)}(s-1)-\sum_{n=2}^{N+1} g_n^{(s)}\left(\frac{\epsilon_n^{s-1}(\epsilon_n-\epsilon_1)}{\epsilon_n+\omega}\right)\right]$$

$$=\sum_{n=1}^{N+1} g_n^{(s)}\left(\frac{\epsilon_n^{s-1}}{\epsilon_n+\omega}\right). \tag{48b}$$

Note the resemblance among Eqs. (44), (48a), and (48b); the effective spectra $\{\varepsilon_n, f_n^{(s)}\}$ and $\{\epsilon_n, g_n^{(s)}\}$ give variationally optimized bounds on $G^{(s)}(\omega)$ for *any* ω.

A relation between $L(\mu)$ and $G^{(s)}(\omega)$

$$L(\mu)=\lim_{\omega\to\infty}\left(S(\mu)\ln\omega+\sum_{l=1}^{\mu-s+1} S(\mu-l)\frac{(-\omega)^l}{l}-\int_0^{\omega}(-\omega)^{\mu-s+1}G^{(s)}(\omega)d\omega\right) \tag{49}$$

is derived in Appendix B for $\mu<\frac{3}{2}$, $s<\frac{5}{2}$, and $\mu-s=-1,0,1,\ldots$. Substitution of $J_{\max}(\omega)$ of Eq. (48a) or $I_{\min}(\omega)$ of Eq. (48b) for $G^{(s)}(\omega)$ of Eq. (49) leads to a variationally optimized bound on $L(\mu)$. On the other hand, a straightforward algebra shows that

$$L^{(s)}(\mu)=\lim_{\omega\to\infty}\left(S^{(s)}(\mu)\ln\omega+\sum_{l=1}^{\mu-s+1} S^{(s)}(\mu-l)\frac{(-\omega)^l}{l}-\int_0^{\omega}(-\omega)^{\mu-s+1}J_{\max}(\omega)d\omega\right). \tag{50a}$$

By comparison between Eqs. (49) and (50a), we see that $L^{(s)}(\mu)$ is a variational lower bound on $L(\mu)$ for even values of $\mu-s$ and a variational upper bound for odd values of $\mu-s$, if $S^{(s)}(\nu)=S(\nu)$ for $\nu=s-1$, $s,\ldots,\mu$. This condition is satisfied for $\mu=s-1$ and s [Eq. (18)]. Therefore, inequalities (19) have been proved. If $s=0$ and $\varphi^{(2)}$, as well as $\varphi^{(0)}$, is included in the basis set, then both Eq. (18) and Eq. (20) hold; $S^{(0)}(\nu)=S(\nu)$ for $\nu=-1$, 0, 1, and 2. Therefore, inequalities (21) follow.

For the effective spectrum $\{\epsilon_n, g_n^{(s)}\}$, it follows that

$$\mathcal{L}^{(s)}(\mu)=\lim_{\omega\to\infty}\left(\mathcal{S}^{(s)}(\mu)\ln\omega+\sum_{l=1}^{\mu-s+1}\mathcal{S}^{(s)}(\mu-l)\frac{(-\omega)^l}{l}-\int_0^{\omega}(-\omega)^{\mu-s+1}I_{\min}(\omega)d\omega\right). \tag{50b}$$

Comparison between Eqs. (49) and (50b) shows that $\mathcal{L}^{(s)}(\mu)$ is a variational upper bound on $L(\mu)$ for even values of $\mu-s$ and a variational lower bound for odd values of $\mu-s$, if $\mathcal{S}^{(s)}(\nu)=S(\nu)$ for $\nu=s-1,s,\ldots,\mu$. This condition is satisfied for $\mu=s-1$, s, and $s+1$ [Eq. (30)]. Thus, inequalities (31) have been proved.

The bounds obtained by Shimamura and Watanabe[13] are equivalent to those of this section. However, their formulation has been given only for $s=0$ and $\mu=-1$, 0, 1, and 2, and for $s=2$ and $\mu=1$ and 2. Their bounds are expressed as infinite series in terms of $\underline{B}^{-1}\underline{A}$ and $\underline{W}^{-1}\underline{V}$, and are inconvenient for computational purposes. On the other hand, the expressions (17b) and (29b) for the bounds have simple forms that give an additional insight into the bounds.

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APPENDIX A: PROOF OF EQS. (18) AND (30)

From the eigenvalue problem (12) and the orthonormalization condition $\underline{c}_n^T\underline{B}\underline{c}_m=\delta_{nm}$, it follows that

$$\sum_{n=1}^{N}\underline{c}_n\underline{c}_n^T=\underline{B}^{-1} \tag{A1}$$

and that

$$\sum_{n=1}^{N}\underline{c}_n\epsilon_n\underline{c}_n^T=\underline{B}^{-1}\underline{A}\underline{B}^{-1}\ . \tag{A2}$$

According to Eqs. (17a) and (16b) we have

$$S^{(s)}(s-1)=\sum_{n=1}^{N}[\underline{B}\underline{c}_n\underline{c}_n^T\underline{B}]_{11}=B_{11} \tag{A3}$$

and

$$S^{(s)}(s)=\sum_{n=1}^{N}[\underline{B}\underline{c}_n\underline{c}_n^T\underline{B}]_{11}\epsilon_n=A_{11}\ , \tag{A4}$$

where Eqs. (A1) and (A2) have been used to derive the second equalities of Eqs. (A3) and (A4). From definitions (11a) and (11b) of $\underline{A}$ and $\underline{B}$, the choice that u_1 is $\varphi^{(s)}$ of Eq. (9), and formula (15) for $S(\mu)$, we obtain

$$B_{11}=S(s-1)\text{ and }A_{11}=S(s)\ , \tag{A5}$$

and therefore, Eqs. (18). Equations (20) have been derived by Dalgarno and Epstein[32] under the condition that both $\varphi^{(0)}$ and $\varphi^{(2)}$ are included in the basis set.

For the eigenvalue problem (22), relations similar to Eqs. (A1) and (A2) are

$$\sum_{n=2}^{N+1}\underline{d}_n\underline{d}_n^T=\underline{W}^{-1} \tag{A6}$$

and

$$\sum_{n=2}^{N+1}\underline{d}_n\epsilon_n\underline{d}_n^T=\underline{W}^{-1}\underline{V}\underline{W}^{-1}\ . \tag{A7}$$

We define two new quantities $R(\mu)$ and $\mathcal{R}^{(s)}(\mu)$ by

$$R(\mu)=S(\mu)-E_{01}S(\mu-1) \tag{A8}$$

and

$$\mathcal{R}^{(s)}(\mu)=\mathcal{S}^{(s)}(\mu)-\epsilon_1\mathcal{S}^{(s)}(\mu-1)\ . \tag{A9}$$

A discrete oscillator strength at E_1, if any, contributes nothing to $R(\mu)$ or $\mathcal{R}^{(s)}(\mu)$. Therefore, it follows from Eqs. (29a), (27b), (A6), (23b), and (A5) that

$$\mathcal{R}^{(s)}(s)=\sum_{n=2}^{N+1}(\underline{W}\underline{d}_n\underline{d}_n^T\underline{W})_{11}=W_{11}=R(s)\ . \tag{A10}$$

In a similar manner we obtain a relation

$$\mathcal{R}^{(s)}(s+1)=\sum_{n=2}^{N+1}(\underline{W}\underline{d}_n\underline{d}_n^T\underline{W})_{11}\epsilon_n$$
$$=V_{11}=R(s+1)\ . \tag{A11}$$

These two relations, combined with the first of Eqs. (30), lead to the other two of Eqs. (30). The first one follows from Eqs. (28) and (29a).

APPENDIX B: DERIVATION OF EQ. (49)

From Eq. (44) we have

$$\int_0^\omega (-\omega)^{\mu-s+1}G^{(s)}(\omega)d\omega = \int_0^\omega \left[\sum_n f_n E_{0n}^{s-1}\left(\frac{E_{0n}^{\mu-s+1}}{(E_{0n}+\omega)} - \sum_{l=0}^{\mu-s} E_{0n}^{\mu-s-l}(-\omega)^l\right)\right]d\omega$$

$$= S(\mu)\ln\omega + P(\mu;\omega) - L(\mu) + \sum_{l=1}^{\mu-s+1} S(\mu-l)\frac{(-\omega)^l}{l} \tag{B1}$$

for $\mu<\frac{5}{2}$, $s<\frac{5}{2}$, and $\mu-s=-1, 0, 1, 2, \ldots$, where

$$P(\mu;\omega)=\sum_n f_n E_{0n}^{\mu}\ln\left(1+\frac{E_{0n}}{\omega}\right) . \tag{B2}$$

For $\mu=s-1$, the sum over l vanishes. Consider a quantity

$$\lim_{\omega\to\infty}\left(S(\mu)\ln\omega + P(\mu;\omega) + \sum_{l=1}^{\mu-s+1} S(\mu-l)\frac{(-\omega)^l}{l} - \int_0^\omega (-\omega)^{\mu-s+1}G^{(s)}(\omega)d\omega\right) . \tag{B3}$$

The expression in the large parentheses is equal to $L(\mu)$ according to Eq. (B1). Because $L(\mu)$ is independent of ω, so is this expression. Therefore, its limit (B3) as $\omega\to\infty$ remains equal to $L(\mu)$. Then, Eq. (49) is proved, if the limit of $P(\mu;\omega)$ is shown to vanish as $\omega\to\infty$.

In taking this limit, one must avoid simply interchanging the order of the limit $\omega\to\infty$ and the summation over n, because E_{0n} tends to infinity as $n\to\infty$. We use the fact[1,3] that

$$\frac{df}{dE} = \alpha E^{-7/2} + (\text{higher-order terms}) , \tag{B4}$$

which holds for $E\geq E_c$ if the constant E_c is chosen sufficiently large. The summation in Eq. (B2) may be split into two parts as

$$\lim_{\omega\to\infty} P(\mu;\omega) = \lim_{\omega\to\infty}\sum^{E_c} f_n E_{0n}^{\mu}\ln\left(1+\frac{E_{0n}}{\omega}\right) + \lim_{\omega\to\infty}\int_{E_c}^\infty \alpha E^{\mu-(7/2)}\ln\left(1+\frac{E}{\omega}\right)dE . \tag{B5}$$

The first term in Eq. (B5) vanishes. The second term may be written, after partial integration, as

$$\lim_{\omega\to\infty}\left[\left(\frac{2\alpha}{5-2\mu}\right)E_c^{\mu-(5/2)}\ln\left(1+\frac{E_c}{\omega}\right) + \left(\frac{2\alpha}{5-2\mu}\right)\int_{E_c}^\infty \frac{dE}{E^{(5/2)-\mu}(E+\omega)}\right] = \frac{2\alpha}{5-2\mu}\lim_{\omega\to\infty}\int_{E_c}^\infty \frac{dE}{E^{(5/2)-\mu}(E+\omega)}$$

$$\equiv \frac{2\alpha}{5-2\mu}\lim_{\omega\to\infty} Q(\mu;E_c,\omega) . \tag{B6}$$

For $\mu<\frac{3}{2}$, $Q(\mu;E_c,\omega)$ vanishes as ω^{-1} or faster as $\omega\to\infty$, because

$$0 \leq \lim_{\omega\to\infty} Q(\mu;E_c,\omega)$$

$$\leq \lim_{\omega\to\infty}\int_{E_c}^\infty \frac{dE}{E^{(5/2)-\mu}\omega} = \lim_{\omega\to\infty}\frac{\text{const}}{\omega} . \tag{B7}$$

More generally, for any $\mu<\frac{5}{2}$, we have

$$0 \leq Q(\mu;E_c,\omega) \leq \int_{E_c}^\infty \frac{dE}{E^{(7/2)-\mu}} = \frac{2}{5-2\mu}E_c^{-(5/2-\mu)} . \tag{B8}$$

This quantity may be made as small as desired, because one may choose any large constant value of E_c. This concludes the proof of Eq. (49), which is a generalization of the Appendix of Ref. 13.

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