PHYSICAL REVIEW A VOLUME 31, NUMBER 4 APRIL 1985

Applications of exponential interpolation to the computation of moment-theory bounds on second-order perturbation expressions

Michael C. Struensee
Department of Physics, University of Texas at Austin, Austin, Texas 78712

(Received 8 August 1984)

It is shown that Prony's method of exponential interpolation provides a simple technique for the construction of effective oscillator-strength distributions from a set of moments of the actual distribution. These effective oscillator-strength distributions may then be inserted into second-order perturbation expressions to yield upper and lower bounds on properties of atoms and molecules. Extensive calculations have been performed on the ground state of atomic hydrogen and bounds on the logarithmic mean excitation energies and the van der Waals coefficient are obtained.

I. INTRODUCTION

Many properties of atoms and molecules arise from second-order perturbation theory due to some kind of electric dipole interaction. In these cases the property can be written as a perturbation expression involving a sum over the dipole oscillator strengths between states and the associated energy differences. Examples of these dipole interaction expressions include the static and dynamic polarizability, the Verdet constant, the coefficient of the $1/R^6$ term in the van der Waals interaction energy, and also the logarithmic mean excitation energies required for calculations of the Lamb shift and collisions of fast charged particles with atoms and molecules.

The difficulty in a straightforward evaluation of the perturbation expression, of course, arises from the fact that all oscillator strengths (i.e., all states of symmetry allowed by selection rules) must be known. This is possible to do explicitly only with the hydrogen atom. Accurate variational calculations for atomic and molecular states are possible only for low-lying bound states, which by themselves are not sufficient to allow evaluation of the perturbation expressions. Variational approaches to the evaluation of the perturbation expressions may be formulated which do not require knowledge of the individual states. These variational techniques provide one powerful approach for evaluating the perturbation expressions; however, this paper will instead follow the approach which relies upon the theory of moments.

The problem of the requirement of complete knowledge of all states can be overcome to some extent by the use of dipole oscillator-strength sums. Dipole oscillator-strength sums $S(k)$ are moments of the dipole oscillator-strength distribution. For $k=2,1,0,-1$ these sums are calculable as ground-state expectation values and for $k=-2,-4,-6$ they can be deduced from experiment. It has been shown earlier[1] that these sums can be used to construct an effective distribution of states (which consists of a collection of effective dipole oscillator strengths and associated energies). The perturbation expressions may be evaluated with this effective distribution to yield upper and lower bounds on various physical properties.

The construction of the effective distribution has been described elsewhere,[1] but here a simplified solution is presented, based on Prony's method of exponential interpolation.[2] An immediate consequence is a closed-form solution for an upper bound to the static polarizability in terms of $S(-1)$, $S(0)$, $S(1)$, and ω_1, the energy difference between the ground state and the lowest excited state having nonvanishing oscillator strength with the ground state. Various bounding properties are discussed and illustrated with extensive calculations which have been carried out on the hydrogen atom.

II. PERTURBATION THEORY AND DIPOLE OSCILLATOR-STRENGTH DISTRIBUTIONS

The properties of primary interest here are the dynamic polarizability, the Verdet constant, the coefficient of the $1/R^6$ term in the van der Waals interaction energy, and the logarithmic mean excitation energies. The perturbation expressions corresponding to these properties have different functional dependences upon the oscillator-strength distribution, yet the effective distributions to be constructed will yield bounds on all of these expressions. The pertinent physical quantities shall be briefly described below. For more details the reader is referred to the comprehensive review articles by Fano and Cooper[3] and Hirschfelder, Byers-Brown, and Epstein.[4]

The dipole oscillator strength between state $|n\rangle$ and state $|b\rangle$ is defined by

$$f_{nb}=\frac{2}{3}\left[\left|\left\langle n\left|\sum_{\mu}x_{\mu}\right|b\right\rangle\right|^2+\left|\left\langle n\left|\sum_{\mu}y_{\mu}\right|b\right\rangle\right|^2+\left|\left\langle n\left|\sum_{\mu}z_{\mu}\right|b\right\rangle\right|^2\right]\omega_{nb}\ , \qquad (1)$$

where $\omega_{nb}=E_b-E_n$ and the summation over μ ranges over all electrons of the atom or molecule. Atomic units are used throughout this work. Many second-order properties of the ground state $|0\rangle$ of an atom or molecule may be evaluated once f_{0b} and ω_{0b} are known for all states $|b\rangle$. The oscillator strength between the ground state and the excited states may be plotted as a function of ω_{0b} consisting of δ function spikes for transitions with the bound states (beneath the first ionization threshold) and an actual function for transitions with the scattering states (above the first ionization threshold). This "function" of ω_{0b} shall be termed the dipole oscillator-strength distribution.

The dipole oscillator-strength distribution may be characterized by its moments with respect to the energy. The dipole oscillator-strength sum of order k is defined by

$$S(k)=\sum_b f_{0b}(\omega_{0b})^k \tag{2}$$

and is simply the kth moment of the oscillator-strength distribution with respect to the energy difference with the ground state. These moments are of interest because for $k=2,1,0,-1$ they can be calculated from ground-state expectation values and for $k=-2,-4,-6$ they can be deduced from experiment.

The orientation-averaged dynamic polarizability $\alpha(\omega)$ (in response to a driving frequency ω) is given by the expression

$$\alpha(\omega)=\sum_b \frac{f_{0b}}{\omega_{0b}^2-\omega^2} . \tag{3}$$

The polarizability $\alpha(\omega)$ may be used to evaluate the Rayleigh scattering cross section and the frequency-dependent index of refraction. For low driving frequencies ω, a simple expansion allows (3) to be rewritten in the Cauchy expansion form

$$\alpha(\omega)=\sum_{k=0}^{\infty} S(-2-2k)\omega^{2k} \tag{4}$$

which converges for ω less than the lowest transition frequency. The Verdet constant, which characterizes the Faraday effect, is another frequency-dependent property which can be written in terms of oscillator strengths. The Verdet constant is proportional to $\beta(\omega)$, where

$$\beta(\omega)=\sum_b \frac{f_{0b}\omega^2}{(\omega_{0b}^2-\omega^2)^2} . \tag{5}$$

A Cauchy expansion for $\beta(\omega)$ can be easily obtained.

The coefficient $C_{\gamma\delta}$ of the $1/R^6$ term in the van der Waals interaction energy between two spherically symmetric ground-state atoms γ and δ is due to a dipole-dipole interaction. Using second-order perturbation theory it is found that

$$C_{\gamma\delta}=\frac{3}{2}\sum_m \sum_n \frac{f_{0m}(\gamma)f_{0n}(\delta)}{[\omega_{0m}(\gamma)+\omega_{0n}(\delta)]\omega_{0m}(\gamma)\omega_{0n}(\delta)} . \tag{6}$$

Note that the summations range over the oscillator-strength distributions of both atom γ and atom δ.

The logarithmic mean excitation energies are defined[5] by

$$L(k)=\sum_b f_{0b}(\omega_{0b})^k \ln(\omega_{0b}) . \tag{7}$$

These are required for the following computations.

(1) Small-angle scattering of fast charged particles with atoms and molecules.

(a) $L(-1)$, for total inelastic scattering cross sections—Inokuti *et al.*,[6] 1967.

(b) $L(0)$, for stopping power (mean energy loss)—Bethe,[7] 1930.

(c) $L(1)$, for straggling (mean fluctuation of energy loss)—Fano,[8] 1963.

(2) $L(2)$, for the Lamb shift—Bethe,[9] 1947.

Note that $L(2)$ is also of interest for excited states. In this case the definition of $L(2)$ requires that the absolute value of the argument of the logarithm be taken, but excited states will not be considered here. It is easily seen from Eqs. (2) and (7) that $L(k)$ is merely the slope of $S(k)$, i.e.,

$$L(k)=\left.\frac{d}{dx}S(x)\right|_{x=k} . \tag{8}$$

III. EVALUATION OF DIPOLE OSCILLATOR-STRENGTH SUMS

In this section the techniques used to obtain the set of $S(k)$ required to construct the effective distribution shall be reviewed. If a good wave function is available it is possible to compute accurate values of $S(k)$ for $k=2,1,0,-1$ using the so-called "sum rules." Measurements of the refractive index and the Verdet constant over a range of frequencies allows the determination of $S(k)$ for $k=-2,-4,-6$ and $k=-4,-6$, respectively.

The well known sum rules[3,10] express $S(2)$, $S(1)$, $S(0)$, and $S(-1)$ in terms of expectation values of the wave function. Given an accurate wave function, these sums may be readily computed. For a state $|\psi\rangle$ $S(k)$ can be written as

$$S(2)=\frac{4\pi}{3}\sum_\alpha Z_\alpha \left\langle \psi \left| \sum_{j=1}^{N} \delta(\mathbf{r}_{j\alpha}) \right| \psi \right\rangle , \tag{9}$$

$$S(1)=\frac{2}{3}\left\langle \psi \left| \left[\sum_{j=1}^{N} \mathbf{p}_j \right]^2 \right| \psi \right\rangle , \tag{10}$$

$$S(0)=N , \tag{11}$$

$$S(-1)=\frac{2}{3}\left\langle \psi \left| \left[\sum_{j=1}^{N} \mathbf{r}_j \right]^2 \right| \psi \right\rangle , \tag{12}$$

where $\mathbf{r}_j$ is the position operator, $\mathbf{p}_j$ is the momentum operator, the index j ranges over the N electrons, and α ranges over the nuclei with atomic number Z_α. Sum rules for $S(3)$, $S(4)$, $S(5)$, ... may also be derived,[11] but are not useful for atomic and molecular ground states because $S(k)$ diverges at $k=2.5$ for these wave functions. This is easily shown for atoms by the following argument. The value of $S(2)$ for a ground state must be greater than zero if it has a nonvanishing oscillator-strength spectrum. This is because for a ground state all f_{0n} and ω_{0n} must be positive, which, of course, implies that $S(2)=\sum_n f_{0n}\omega_{0n}^2$ must also be positive. The divergence at $k=2.5$ follows from the behavior of the oscillator strength in the continuum at high energies. The oscillator-strength density between the ground state and the continuum states of energy

ϵ, denoted by $df/d\epsilon$, has, for atoms, the asymptotic form given by[12]

$$\frac{df}{d\epsilon}=\frac{2\sqrt{2}Z}{\pi}S(2)\epsilon^{-3.5}-2Z^2S(2)\epsilon^{-4}+\cdots \; . \tag{13}$$

Clearly if $S(2)\neq 0$ then the continuum integration contribution to $S(k)$,

$$\int^{\infty}\frac{df}{d\epsilon}(\epsilon-E_0)^k \; ,$$

will cause $S(k)$ to diverge at $k=2.5$. A similar argument may be used to show that $S(k)$ diverges at $k=2.5$ for molecular ground states.

Alternative methods are needed to obtain $S(k)$ for k other than $-1,0,1,2$. The static polarizability [which is just $S(-2)$] can be accurately obtained using variational perturbation methods. This is sometimes considered a sum rule because it can be calculated without explicit reference to physical oscillator strengths. The static polarizability can also be accurately measured. Variational calculations may be used to compute $S(-3)$, $S(-4)$, $S(-5)$, etc., however it is difficult to assess the accuracy of these calculations.[13] From experimental refractive index and Faraday-effect measurements it is possible to extract $S(-2)$, $S(-4)$, and $S(-6)$. This is accomplished by performing a polynomial least-squares fit to the data to obtain the coefficients in the Cauchy expansions for $\alpha(\omega)$ and $\beta(\omega)$.[14]

IV. CONSTRUCTION OF THE EFFECTIVE OSCILLATOR-STRENGTH DISTRIBUTION

Once an accurate set of $S(k)$ has been obtained, the effective distribution may be constructed. The effective distribution consists of a finite number of discrete "states," each having an associated oscillator strength and energy difference with the wave function of interest (usually the ground state). The construction of N effective states requires the specification of $2N$ parameters, the N effective oscillator strengths and the associated N effective energy differences. There are many conceivable ways of constructing the effective set of states, but only two of these prove to be useful for the purpose of bounding perturbation expressions. The effective states are constructed by demanding that the effective distribution satisfies the set of known $S(k)$. This results in a system of $2N$ algebraic equations which must be solved to obtain the N effective oscillator strengths f'_{nb} and the associated N energy differences ω'_{nb} with the state of interest $|n\rangle$ (note $b=1,2,\ldots,N$). An effective state $|b\rangle'$ is completely specified by knowledge of f'_{nb} and ω'_{nb}.

Before describing the two methods of construction it should be emphasized that the effective distribution will provide bounds only if the actual distribution from which the $S(k)$ are being obtained has no negative energy differences (and therefore no negative oscillator strengths). Clearly if the state of interest $|n\rangle$ is the ground state there is no problem. However, for excited states it is possible to have nonvanishing dipole matrix elements with lower energy states $|a\rangle$, which results in oscillator strengths in the distribution associated with negative ω_{na}. The problem can be eliminated by applying the method described here to only the "modified oscillator-strength distribution" which consists of only those states $|a\rangle$ such that $E_a>E_n$. In order to carry the procedure through, the actual oscillator strengths and energy differences for the states $|a\rangle$ with $E_a<E_n$ must be known. To construct the "effective modified oscillator-strength distribution" one must use "modified" $S_m(k)$ which are obtained from the usual $S(k)$ by subtracting the contributions of the physical states $|a\rangle$ which satisfy $E_a<E_n$, i.e.,

$$S_m(k)=S(k)-\sum_{\substack{a\\E_a<E_n}} f_{na}\omega_{na}^k \; . \tag{14}$$

Using a set of $S_m(k)$ allows the construction of an effective modified oscillator-strength distribution in the same way that $S(k)$ allows the construction of an effective oscillator-strength distribution. However, upon evaluating the perturbation expressions for which bounds are desired one must include not only the effective modified oscillator-strength distribution, but also explicitly include the oscillator-strength distribution for states $|a\rangle$ with $E_a<E_n$. In other words, a set of physical oscillator strengths and energy differences must be explicitly included and then the technique described in this work is used to provide bounds on the "remainder term." In fact even if negative oscillator strengths are not a problem (e.g., the ground state) and oscillator strengths and energy differences for some low-lying states are known, the above procedure should be followed to improve accuracy. The more physical states which are included, the less significant will be the remainder term one must bound. For simplicity the following discussion shall assume $|n\rangle$ is the ground state and physical oscillator strengths are not known. If this is not the case, the above technique may be used to modify the treatment. In the following, f'_{0b} and ω'_{0b} shall be denoted by f'_b and ω'_b, respectively.

The two methods of constructing effective oscillator-strength distributions using a set of $S(k_i)$ are the following.

(1) Construction from a set of $S(k_i)$, $i=1,2,\ldots,2N$. The effective distribution f'_b, ω'_b, $b=1,2,\ldots,N$, is determined by the system of equations

$$S(k_i)=\sum_{b=1}^{N} f'_b(\omega'_b)^{k_i} \; , \quad i=1,2,\ldots,2N \; . \tag{15}$$

(2) Construction from a set of $S(k_i)$, $i=1,2,\ldots,2N-1$ and also knowledge of E_1, the energy of the lowest excited state with which the ground state has a nonvanishing oscillator strength. The effective distribution f'_b,ω'_b, $b=1,2,\ldots,N$ is determined by the system of equations

$$S(k_i)=\sum_{b=1}^{N} f'_b(\omega'_b)^{k_i} \; , \quad i=1,2,\ldots,2N-1 \tag{16}$$

and $\omega'_1=E_1-E_0$.

The bounding behavior is a consequence of the fact that the effective distribution has been given the minimum number of degrees of freedom needed to satisfy the equations. In case (1) the effective distribution has $2N$ parameters (f'_b,ω'_b) which are specified by the $2N$ $S(k_i)$. In case (2) the effective distribution has $2N-1$ free parameters (f'_b, $b=1,2,\ldots,N$ and ω'_b, $b=2,3,\ldots,N$) which are specified once $2N-1$ $S(k_i)$ are known. The bounding behavior of these distributions will be described later, but the immediate interest is the solution of these equations.

For the general case of $S(k_i)$ known for an arbitrary set of k_i, iterative numerical procedures must be applied in order to solve the system of equations (15) or (16). However, a more systematic solution is possible for the frequently occurring case of regularly spaced k_i, e.g., integrally spaced k_i ($k_i=k_0+i$) or double integrally spaced k_i ($k_i=k_0+2i$). Gordon[15] managed to turn the problem into one of diagonalizing a tridiagonal matrix with entries constructed from the $S(k_i)$ by using recursion relations obtained from the theory of continued fractions. Another description of this technique is found in Wheeler and Gordon.[16] Luyckx *et al.*[17] formulate case (1) in terms of an eigenvalue problem without the need for continued-fraction theory. Shimamura and Inokuti[5] solve case (1) essentially the same as Luyckx, *et al.*, but also are able to solve case (2) in a similar fashion as an eigenvalue problem. Here a further simplification over these previous solutions is presented.

The following solution is based on Prony's method of exponential interpolation.[2] This approach allows the immediate construction of an Nth-degree polynomial with coefficients in the form of determinants with the $S(k)$ as entries. The zeros of the polynomial will be the effective energy differences ω'_b. Once the ω'_b are known, the problem is easily reduced to a linear system of equations which can be solved to obtain the effective oscillator strengths f'_b. This technique is directly applicable to case (1) and with minor modification can be used for case (2).

Following Whittaker and Robinson,[18] Prony's method of exponential interpolation shall be explained in terms of case (1). Recall that the system of equations which must be solved is

$$\begin{aligned} S(k_1)&=\sum_{b=1}^{N} f'_b(\omega'_b)^{k_1}\ ,\\ S(k_2)&=\sum_{b=1}^{N} f'_b(\omega'_b)^{k_2}\ ,\\ &\ \ \vdots\\ S(k_{2N})&=\sum_{b=1}^{N} f'_b(\omega'_b)^{k_{2N}}\ . \end{aligned} \tag{15'}$$

An effective dipole oscillator-strength sum $S'(k)$, a continuous function of k, may clearly be defined by

$$S'(k)=\sum_{b=1}^{N} f'_b(\omega'_b)^k \tag{17}$$

which satisfies the equations

$$S'(k_i)=S(k_i)\ ,\quad i=1,2,\ldots,2N\ . \tag{18}$$

For convenience the following derivation shall assume that the k_i for which $S(k_i)$ is known are integrally spaced, i.e., $k_i=k_0+i$, where $i=1,2,\ldots,2N$. $S'(k+i)$ can be written as

$$S'(k+i)=\sum_{b=1}^{N}[f'_b(\omega'_b)^i](\omega'_b)^k$$

hence

$$F_i(k)=\sum_{b=1}^{N} c_{ib}G_b(k)\ , \tag{17'}$$

where

$$\begin{aligned} &F_i(k)=S'(k+i)\ ,\\ &G_b(k)=(\omega'_b)^k\ ,\\ &c_{ib}=f'_b(\omega'_b)^i\ . \end{aligned}$$

Note that the $G_b(k)$ for $b=1,2,\ldots,N$ are linearly independent functions of k if the ω'_b are nondegenerate. Also note that the effective energy differences ω'_b are nondegenerate (or equivalently, at least one effective oscillator strength is zero) only if the original oscillator-strength distribution consists of less than N discrete states. Since this never happens physically, the N $G_b(k)$ for the problem under consideration will be linearly independent as functions of k (one must also assume that $\omega'_b\neq 0$, but this is never a problem). Given the above restrictions $f'_b\neq 0$, $\omega'_b\neq 0$, and ω'_b nondegenerate for $b=1,2,\ldots,N$, it shall be shown that the $F_i(k)$ for $i=1,2,\ldots,N$, comprise N linearly independent functions of k. This is easily proven by checking that the square matrix c_{ib} defined in Eq. (17′) is indeed nonsingular, i.e., the determinant is nonzero:

$$\det(c_{ib})=\begin{vmatrix} f_1\omega_1 & f_2\omega_2 & \cdots & f_N\omega_N\\ f_1\omega_1^2 & f_2\omega_2^2 & \cdots & f_N\omega_N^2\\ \vdots & \vdots & & \vdots\\ f_1\omega_1^N & f_2\omega_2^N & \cdots & f_N\omega_N^N \end{vmatrix}$$

$$=f_1f_2\cdots f_N\omega_1\omega_2\cdots\omega_N\begin{vmatrix} 1 & 1 & \cdots & 1\\ \omega_2 & \omega_1 & \cdots & \omega_N\\ \vdots & \vdots & & \vdots\\ \omega_1^{N-1} & \omega_2^{N-1} & \cdots & \omega_N^{N-1} \end{vmatrix}$$

$$=f_1f_2\cdots f_N\omega_1\omega_2\cdots\omega_N(\omega_N-\omega_{N-1})(\omega_N-\omega_{N-2})\times\cdots\times(\omega_N-\omega_1)$$
$$\times(\omega_{N-1}-\omega_{N-2})(\omega_{N-1}-\omega_{N-3})\times\cdots\times(\omega_{N-1}-\omega_1)\times\cdots\times(\omega_2-\omega_1)\ ,$$

where the last step has been performed by the difference-product expansion of the alternant determinant.[19] Written in this form, the determinant is obviously nonzero for f_b' and ω_b' satisfying the previous restrictions, hence the $F_i(k)$ for $i=1,2,\ldots,N$ are linearly independent functions of k. Now consider the function $F_0(k)=S'(k)=\sum_b f_b'(\omega_b')^k$. As functions of k the set $F_0(k), F_1(k),\ldots,F_N(k)$ must clearly be linearly dependent. Therefore there exist unique (up to an overall scale) α_j such that

$$\alpha_0F_0(k)+\alpha_1F_1(k)+\cdots+\alpha_NF_N(k)=0$$

or equivalently

$$\alpha_0S'(k)+\alpha_1S'(k+1)+\cdots+\alpha_NS'(k+N)=0\ . \tag{19}$$

The α_j can be determined using the known $S(k_i)$, $i=1,2,\ldots,2N$, as will be described. Once the α_j are known, the above equation can be rewritten

$$\alpha_0\sum_{b=1}^{N}f_b'(\omega_b')^k+\alpha_1\sum_{b=1}^{N}f_b'(\omega_b')^{k+1}+\cdots+\alpha_N\sum_{b=1}^{N}f_b'(\omega_b')^{k+N}=0 \tag{20}$$

or

$$\sum_{b=1}^{N}[\alpha_N(\omega_b')^N+\alpha_{N-1}(\omega_b')^{N-1}+\cdots+\alpha_0]f_b'(\omega_b')^k=0\ . \tag{20'}$$

Since the $(\omega_b')^k$ are linearly independent functions of k, the above equation can be satisfied only if each coefficient is identically zero, which means all of the N ω_b' must satisfy the polynomial equation

$$\alpha_N(\omega_b')^N+\alpha_{N-1}(\omega_b')^{N-1}+\cdots+\alpha_0=0\ . \tag{21}$$

Therefore once the α_j have been found all that remains is to determine the roots of Eq. (21) in order to obtain the N effective energy differences ω_b'. The α_j may be determined using Eq. (19) in conjunction with the known $S(k_i)$ where $k_i=k_0+i$, $i=1,2,\ldots,2N$ [recall that it was assumed that the $S(k_i)$ were known for integrally spaced k_i]. Utilizing Eq. (19), N simultaneous equations are constructed by replacing k with $k_0+1,k_0+2,\ldots,k_0+N$. Doing this yields the system

$$\begin{array}{lllll}\alpha_0S'(k_0+1) & +\alpha_1S'(k_0+2) & +\cdots+ & \alpha_NS'(k_0+N+1) & =0,\\ \alpha_0S'(k_0+2) & +\alpha_1S'(k_0+3) & +\cdots+ & \alpha_NS'(k_0+N+2) & =0,\\ \vdots & \vdots & & \vdots & \vdots\\ \alpha_0S'(k_0+2) & +\alpha_1S'(k_0+3) & +\cdots+ & \alpha_NS'(k_0+N+2) & =0.\end{array} \tag{22}$$

From Eq. (18) it follows that for the arguments of $S(k)$ in the above equations $S'(k)=S(k)$ and so Eq. (22) may be rewritten as

$$\begin{array}{lllll}\alpha_0S(k_0+1) & +\alpha_1S(k_0+2) & +\cdots+ & \alpha_NS(k_0+N+1) & =0,\\ \alpha_0S(k_0+2) & +\alpha_1S(k_0+3) & +\cdots+ & \alpha_NS(k_0+N+2) & =0,\\ \vdots & \vdots & & \vdots & \vdots\\ \alpha_0S(k_0+N) & +\alpha_1S(k_0+N+1) & +\cdots+ & \alpha_NS(k_0+2N) & =0\end{array} \tag{23}$$

which is the familiar case of N homogeneous equations in $N+1$ unknowns and the α_j are determined up to an overall scale factor. $S(k)$ is known for all values of k appearing in the above equations and so a solution can be easily obtained for the system which is unique up to an overall scale.. Using Cramer's rule,[19] one way of writing the solution is the following:

$$\alpha_N=\begin{vmatrix}S(k_0+1) & S(k_0+2) & \cdots & S(k_0+N)\\ S(k_0+2) & S(k_0+3) & \cdots & S(k_0+N+1)\\ \vdots & \vdots & & \vdots\\ S(k_0+N) & S(k_0+N+1) & \cdots & S(k_0+2N-1)\end{vmatrix}\ , \tag{24}$$

$$\alpha_{N-1}=-\begin{vmatrix} S(k_0+1) & S(k_0+2) & \cdots & S(k_0+N) \\ S(k_0+2) & S(k_0+3) & \cdots & S(k_0+N+1) \\ \vdots & \vdots & & \vdots \\ S(k_0+N-2) & S(k_0+N-1) & \cdots & S(k_0+2N-3) \\ S(k_0+N-1) & S(k_0+N) & \cdots & S(k_0+2N-2) \\ S(k_0+N+1) & S(k_0+N+2) & \cdots & S(k_0+2N) \end{vmatrix}, \tag{25}$$

etc. The array inside the determinant for α_j is obtained by deleting the jth row from the following array (here the rows are numbered from zero to N).

$$\begin{array}{lcccc} \text{zeroth row:} & S(k_0+1) & S(k_0+2) & \cdots & S(k_0+N) \\ \text{first row:} & S(k_0+2) & S(k_0+3) & \cdots & S(k_0+N+1) \\ \text{second row:} & S(k_0+3) & S(k_0+4) & \cdots & S(k_0+N+2) \\ & \vdots & \vdots & & \vdots \\ N\text{th row:} & S(k_0+N+1) & S(k_0+N+2) & \cdots & S(k_0+2N)\,. \end{array} \tag{26}$$

Also note that the sign preceding the determinant for α_j is given by $(-1)^{N-j}$. Following this procedure has reduced the original problem of solving a system of nonlinear equations into finding the roots of an Nth-degree polynomial with coefficients α_j, $j=0,1,2,\ldots,N$. The roots can be found numerically to give the ω'_b, $b=1,2,\ldots,N$. Once the ω'_b are known, the problem is that of solving a system of linear equations to obtain the f'_b. Note that the equation for ω' can be written more compactly as a determinant:

$$\begin{vmatrix} 1 & S(k_0+1) & S(k_0+2) & \cdots & S(k_0+N) \\ \omega' & S(k_0+2) & S(k_0+3) & \cdots & S(k_0+N+1) \\ \omega'^2 & S(k_0+3) & S(k_0+4) & \cdots & S(k_0+N+2) \\ \vdots & \vdots & \vdots & & \vdots \\ \omega'^N & S(k_0+N+1) & S(k_0+N+2) & \cdots & S(k_0+2N) \end{vmatrix}=0\,. \tag{27}$$

As an example, assume that $S(-3)$, $S(-2)$, $S(-1)$, $S(0)$, $S(1)$, and $S(2)$ are known. One constructs an array according to Eq. (26):

$$\begin{matrix} S(-3) & S(-2) & S(-1) \\ S(-2) & S(-1) & S(0) \\ S(-1) & S(0) & S(1) \\ S(0) & S(1) & S(2) \end{matrix}\,.$$

Using the above procedure the effective energies are obtained by solving

$$\begin{vmatrix} S(-3) & S(-2) & S(-1) \\ S(-2) & S(-1) & S(0) \\ S(-1) & S(0) & S(1) \end{vmatrix}\omega'^3-\begin{vmatrix} S(-3) & S(-2) & S(-1) \\ S(-2) & S(-1) & S(0) \\ S(0) & S(1) & S(2) \end{vmatrix}\omega'^2+\begin{vmatrix} S(-3) & S(-2) & S(-1) \\ S(-1) & S(0) & S(1) \\ S(0) & S(1) & S(2) \end{vmatrix}\omega'-\begin{vmatrix} S(-2) & S(-1) & S(0) \\ S(-1) & S(0) & S(1) \\ S(0) & S(1) & S(2) \end{vmatrix}=0$$

to give $\omega'_1,\omega'_2,\omega'_3$. Then the oscillator strengths f'_1,f'_2,f'_3 are obtained from

$$\begin{bmatrix} f'_1 \\ f'_2 \\ f'_3 \end{bmatrix}=\begin{bmatrix} 1 & 1 & 1 \\ \omega'_1 & \omega'_2 & \omega'_3 \\ \omega_1'^2 & \omega_2'^2 & \omega_3'^2 \end{bmatrix}^{-1}\begin{bmatrix} S(0) \\ S(1) \\ S(2) \end{bmatrix}.$$

The matrix that must be inverted is known as an alternant matrix and closed-form inversion is especially simple.[19]

Case (2) shall be treated by an example. The general treatment follows by analogy. Assume $S(-1)$, $S(0)$, $S(1)$, and ω_1 are known, where $\omega_1=E_1-E_0$ is the actual physical energy difference associated with the lowest physical state having nonvanishing oscillator strength with the ground state. The objective is to construct two effective states such that one of them has ω_1 as its effective energy difference, and in addition the f'_1, f'_2, ω'_1 $(=\omega_1)$, and ω'_2 must satisfy $S(-1)$, $S(0)$, and $S(1)$. The procedure here is similar to that of case (1), but one must first determine the "effective" $S'(-2)$ which allows ω_1 to satisfy the polynomial equation constructed from $S'(-2)$, $S(-1)$, $S(0)$, and $S(1)$ in the usual way for case (1). In order for this to happen $S'(-2)$ must satisfy the equation

$$\begin{vmatrix} S'(-2) & S(-1) \\ S(-1) & S(0) \end{vmatrix}\omega_1^2-\begin{vmatrix} S'(-2) & S(-1) \\ S(0) & S(1) \end{vmatrix}\omega_1+\begin{vmatrix} S(-1) & S(0) \\ S(0) & S(1) \end{vmatrix}=0\,.$$

Solving for $S'(-2)$ one finds

$$S'(-2)=\frac{S(-1)[\omega_1^2 S(-1)-S(1)]-S(0)[\omega_1 S(-1)-S(0)]}{\omega_1[\omega_1 S(0)-S(1)]} . \tag{28}$$

Once $S'(-2)$ is known in terms of $S(-1)$, $S(0)$, $S(1)$, and ω_1 the calculation is performed identically as in case (1), which for this example means one solves for the roots of

$$\begin{vmatrix} S'(-2) & S(-1) \\ S(-1) & S(0) \end{vmatrix} \omega'^2 - \begin{vmatrix} S'(-2) & S(-1) \\ S(0) & S(1) \end{vmatrix} \omega' + \begin{vmatrix} S(-1) & S(0) \\ S(0) & S(1) \end{vmatrix} = 0$$

to obtain ω'_1 and ω'_2. From the construction of $S'(-2)$ it is known that ω_1 must be one of the two roots. Then the oscillator strengths f'_1 and f'_2 can be obtained as usual.

V. UPPER BOUND ON STATIC POLARIZABILITY IN TERMS OF $S(-1)$, $S(0)$, $S(1)$, AND ω_1

Before treating the bounding properties of effective distributions, the importance of Eq. (28) shall be discussed. This equation for $S'(-2)$ is more important than merely an intermediate result in the construction of the effective oscillator-strength distribution. Equation (28) is in fact an upper bound on $S(-2)$, the static polarizability, given a knowledge of $S(-1)$, $S(0)$, $S(1)$, and ω_1.

As mentioned before, an actual sum rule does not exist for $S(-2)$. However, sum rules do exist for $S(-1)$, $S(0)$, and $S(1)$ and note that E_1-E_0 can be accurately obtained from *ab initio* calculations or experiment. Consequently Eq. (28) provides a useful bound on the static polarizability.

The reason for the bounding behavior of Eq. (28) will be deferred until Sec. VI, but first what has been previously known of bounds on the static polarizability, given $S(-1)$, $S(0)$, $S(1)$, $S(2)$, and ω_1, will be described. The fact that the $S(-1)$, $S(0)$, $S(1)$, and ω_1 "constraints" impose the bound has been shown numerically by Futrelle and McQuarrie,[20] however this closed-form expression appears to be a new result. Futrelle and McQuarrie's linear programming technique is more general in the sense that it can be used to incorporate error estimates of the initial data into the final result. The equation presented here, though, is more convenient.

The following list contains four useful bounds $S'(-2)$ on the static polarizability $S(-2)$ in terms of $S(-1)$, $S(0)$, $S(1)$, $S(2)$, and ω_1.

(1) Lower bounds:

$$\text{(a)}S'_{1(\text{a})}(-2)=\frac{[S(-1)]^2}{S(0)} ,$$

$$\text{(b)}S'_{1(\text{b})}(-2)=\frac{S^3(0)+S(2)S^2(-1)-2S(-1)S(0)S(1)}{S(0)S(2)-S^2(1)} .$$

(2) Upper bounds:

$$\text{(a)}S'_{2(\text{a})}(-2)=\frac{S(-1)}{\omega_1} ,$$

$$\text{(b)}S'_{2(\text{b})}(-2)=\frac{S(-1)[\omega_1^2 S(-1)-S(1)]-S(0)[\omega_1 S(-1)-S(0)]}{\omega_1[\omega_1 S(0)-S(1)]} .$$

1(a) and 1(b) yield the same bounds as the case-(1) effective distributions with known $S(-1)$, $S(0)$ and $S(-1)$, $S(0)$, $S(1)$, $S(2)$, respectively. 2(a) and 2(b) yield the same bounds as the case-(2) effective distributions with known $S(-1)$, ω_1 and $S(-1)$, $S(0)$, $S(1)$, ω_1, respectively. Expression 1(a) was first used by Kirkwood[21] and Vinti[22] in 1932. Bound 1(b) was shown by Weinhold[23] in 1968. Bound 2(a) is rather trivial and bound 2(b) is the result presented here.

As an application, bounds on the helium atom polarizability shall be obtained. Pekeris[24] has calculated

$S(2)=30.334$,

$S(1)=4.084$,

$S(0)=2.000$,

$S(-1)=1.505$,

and ω_1 is known[25] to be 0.7797 a.u. Performing the calculations using the preceding equations one finds

$S'_{1(\text{a})}(-2)=1.133$,

$S'_{1(\text{b})}(-2)=1.185$,

$S'_{2(\text{a})}(-2)=1.930$,

$S'_{2(\text{b})}(-2)=1.583$,

as compared with the actual value[26] of $S(-2)=1.383$. The $S'_{1(\text{b})}(-2)$ and $S'_{2(\text{b})}(-2)$ yield tighter bounds than $S'_{1(\text{a})}(-2)$ and $S'_{2(\text{a})}(-2)$, as will always be the case.

The calculation may also be performed by including known oscillator strengths explicitly and using modified oscillator-strength sums. Schiff and Pekeris have calculated[27]

$$f_{1S^1-2P^1}=0.2762\ ,$$

$$f_{1S^1-3P^1}=0.0734\ ,$$

and from Moore's tables[25] one finds (in a.u.)

$$\omega_{1S^1-2P^1}=0.7797\ ,$$

$$\omega_{1S^1-3P^1}=0.8484\ ,$$

$$\omega_{1S^1-4P^1}=0.8725\ .$$

Subtracting the contributions of the first two oscillator strengths, one obtains the modified oscillator-strength sums:

$$S_m(2)=30.113\ ,$$

$$S_m(1)=3.806\ ,$$

$$S_m(0)=1.650\ ,$$

$$S_m(-1)=1.064\ .$$

Computing the four bounds on $S(-2)$ one finds [replacing $S(k)$ by $S_m(k)$ and using $\omega_{1S^1-4P^1}$ for ω_1]:

$$S'_{m\,1(a)}(-2)=0.686\ ,$$

$$S'_{m\,1(b)}(-2)=0.716\ ,$$

$$S'_{m\,2(a)}(-2)=1.219\ ,$$

$$S'_{m\,2(b)}(-2)=0.967\ .$$

Adding the contribution of the first two oscillator strengths to $S(-2)$ yields

$$S'_{1(a)}(-2)=1.242\ ,$$

$$S'_{1(b)}(-2)=1.272\ ,$$

$$S'_{2(a)}(-2)=1.775\ ,$$

$$S'_{2(b)}(-2)=1.523\ ,$$

again, compared with the actual value of $S(-2)=1.383$.

VI. BOUNDING BEHAVIOR OF EFFECTIVE OSCILLATOR-STRENGTH DISTRIBUTIONS

In this section the bounding properties of effective oscillator-strength distributions shall be reviewed. Given an effective distribution it is possible to construct bounds on unknown oscillator-strength sums, logarithmic sums, the coefficient of the $1/R^6$ term in the van der Waals interaction energy, the dynamic polarizability, and the Verdet constant. All of the above bounding properties, with the exception of that of the van der Waals coefficient, are a consequence of the fact that the $S'(k)$ constructed from the effective distribution bounds the actual $S(k)$ in a well-specified manner. The discussion shall begin with a description of this bounding behavior, saving the treatment of the subtler case of the van der Waals coefficient for last. As described previously, the following statements are valid when the original oscillator-strength distribution contains only states for which the energy differences $\omega_{nb}=E_b-E_n$ are greater than zero.

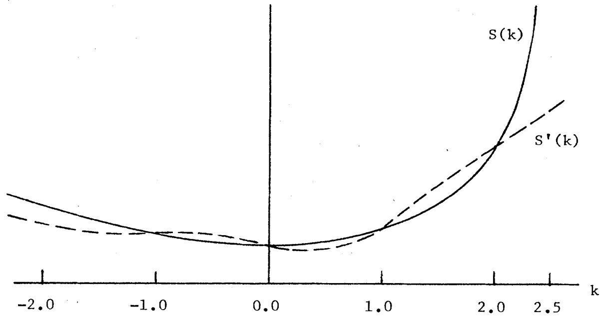

FIG. 1. Schematic of bounding behavior of $S'(k)$ [associated with the effective distribution constructed using $S(2)$, $S(1)$, $S(0)$, and $S(-1)$]. The figure is meant only to represent the qualitative behavior of $S'(k)$; the only relevant information contained in the figure is the relative position of $S(k)$ and $S'(k)$ [i.e., whether $S'(k)$ lies above or below $S(k)$].

The general bounding behavior is indicated in Figs. 1 and 2. In Fig. 1 is shown a typical example of an effective $S'(k)$ constructed from a case-(1) distribution. The effective $S'(k)$ crosses the actual $S(k)$ curve at only those k_i for which $S(k_i)$ was used in the construction of the effective distribution. In Fig. 1 the $S'(k)$ is that which has been obtained from an effective distribution constructed from $S(2)$, $S(1)$, $S(0)$, and $S(-1)$. Another important aspect to note is that to the right of the largest k_i (in this case 2.0) and to the left of the smallest k_i (here -1.0) the effective $S'(k)$ bounds the actual $S(k)$ from below. For the case of regularly spaced k_i, this behavior follows from the discussion of Wheeler and Gordon[16] and Langhoff and Yates.[28] For up to four k_i, Barnsley[29] has shown that this behavior holds even if the k_i are arbitrarily (i.e., not regularly) spaced. The generalization of this behavior for an arbitrarily large number of nonregularly spaced k_i seems likely, although it apparently has not been proven mathematically. In Fig. 2 is shown a typical example of an effective $S''(k)$ constructed from a case-(2) distribution [here constructed from $S(2)$, $S(1)$, $S(0)$, $S(-1)$, $S(-2)$, and ω_1]. Again, the effective $S''(k)$ crosses the actual $S(k)$ curve only at those k_i for which $S(k_i)$ was used in the construction of the effective distribution. In this case,

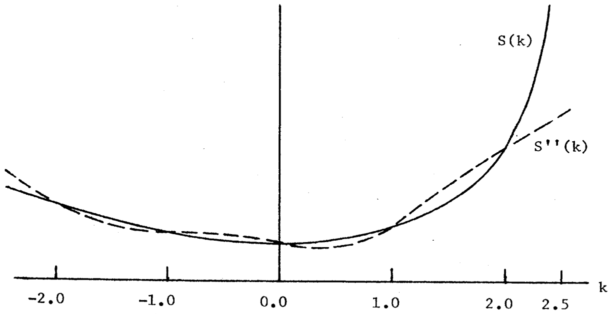

FIG. 2. Schematic of bounding behavior of $S''(k)$ [associated with the effective distribution constructed using $S(2)$, $S(1)$, $S(0)$, $S(-1)$, $S(-2)$, and ω_1].

however, the $S''(k)$ bounds $S(k)$ from above to the left of the smallest k_i [because case-(2) distributions are constructed with an odd number of $S(k_i)$]. For the case of regularly spaced k_i, this behavior follows, as before, from the discussion of Wheeler and Gordon[16] and Langhoff and Yates.[28] Again the generalization for an arbitrarily large number of nonregularly spaced k_i seems likely, but apparently has not been proven.

As an additional example consider a case-(1) distribution constructed from $S(1)$, $S(0)$, $S(-1)$, and $S(-2)$. The behavior of the effective sum $S'''(k)$ constructed from this distribution is illustrated in Fig. 3. Once both $S''(k)$ (in Fig. 2) and $S'''(k)$ (in Fig. 3) are known, both upper and lower bounds have been established on the entire $S(k)$ curve to the left of $k=2.0$. To the left of $k=2.0$, $S''(k)$ and $S'''(k)$ complement one another, $S''(k)$ yielding upper bounds where $S'''(k)$ yields lower bounds and vice versa. To the right of $k=2.0$ both $S''(k)$ and $S'''(k)$ yield only lower bounds on $S(k)$. The usefulness of effective sums from case-(1) and case-(2) distributions has already been illustrated by the bounds derived on the static polarizability in Sec. V.

Knowledge of the bounding behavior of effective sums derived from case-(1) and case-(2) distributions on $S(k)$ allows one to easily determine bounds on the logarithmic sums $L(k_i)$ at those k_i for which $S(k_i)$ was used to construct the effective distribution. First recall that $L(k_i)$ is merely the slope of $S(k)$ at $k=k_i$, i.e.,

$$L(k_i)=\left.\frac{d}{dk}S(k)\right|_{k=k_i} .$$

Similarly, it is easily seen that the effective logarithmic sum $L'(k)$, where $L'(k)=\sum_{b=1}^{N} f_b'(\omega_b')^k \ln(\omega_b')$, is the slope of the effective sum $S'(k)$. Clearly, at those k_i for which $S'(k)$ changes from a lower bound on $S(k)$ on the left of k_i to an upper bound on the right will mean that $L'(k_i)$ is an upper bound to $L(k_i)$. At those k_i for which $S'(k)$ changes from an upper bound on $S(k)$ on the left of k_i to a lower bound on the right will imply that $L'(k_i)$ is a lower bound to $L(k_i)$. From Fig. 2 one sees that $L''(k)$ constructed from this effective distribution will provide an upper bound to $L(-1)$ and $L(1)$ and a lower bound to $L(-2)$, $L(0)$, and $L(2)$. From Fig. 3 one finds that the $L'''(k)$ constructed from this effective distribution will provide an upper bound to $L(-2)$ and $L(0)$ and a lower bound to $L(-1)$ and $L(1)$. Again the distributions complement each other and both upper and lower bounds can be found for all $L(k_i)$ of interest except $L(2)$. For $L(2)$ only lower bounds can be found if no finite $S(k_i)$ are known for $k_i > 2.0$ (which will usually be the case).

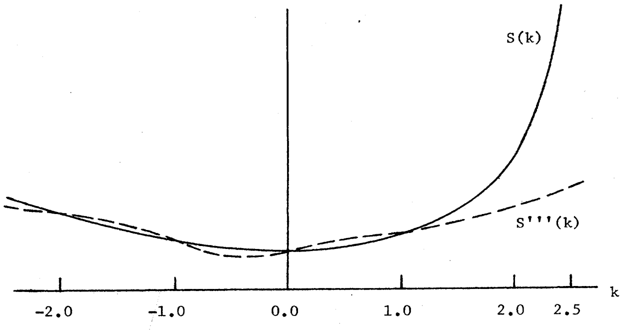

FIG. 3. Schematic of bounding behavior of $S'''(k)$ [associated with the effective distribution constructed using $S(1)$, $S(0)$, $S(-1)$, and $S(-2)$].

Bounds on the dynamic polarizability may also be constructed using effective oscillator-strength distributions. The bounding property of the effective polarizability of the effective polarizability $\alpha'(\omega)$, where

$$\alpha'(\omega)=\sum_{b=1}^{N}\frac{f_b'}{\omega_b'^{\,2}-\omega^2}$$

is valid from $\omega=0$ to the first resonance frequency, the frequency range for which the Cauchy expansion is valid. To understand why bounds hold here, compare the Cauchy expansion of $\alpha'(\omega)$,

$$\alpha'(\omega)=S'(-2)+S'(-4)\omega^2+S'(-6)\omega^4+\cdots ,$$

with that of $\alpha(\omega)$,

$$\alpha(\omega)=S(-2)+S(-4)\omega^2+S(-6)\omega^4+\cdots .$$

Note that a case-(1) effective distribution which satisfies $S'(k_i)\leq S(k_i)$ for $k_i=-2,-4,-6,\ldots$ will generate an effective dynamic polarizability which bounds the actual dynamic polarizability from below. If the case-(1) effective distribution has been constructed from a set which includes certain of the $S(-2)$, $S(-4)$, $S(-6),\ldots$ then those corresponding terms of the Cauchy expansion for $\alpha'(\omega)$ and $\alpha(\omega)$ will be identical. The reason that case-(1) effective distributions must be used for lower bounds is of course that they generate effective $S'(k)$ which bound $S(k)$ from below to the left of the smallest k_i for which $S(k_i)$ has been used in the construction of the distribution. In other words, case-(1) distributions tend to bound the terms which have not been put in explicitly from below, if a reasonable choice of k_i for the construction of the distribution has been made. As an example note that the effective distribution of Fig. 3 satisfies $S(-2)$ "explicitly" and bounds $S(-4)$,$S(-6),\ldots$ from below and and therefore generates an effective dynamic polarizability which bounds the actual dynamic polarizability from below. A similar argument justifies the statement that, with a reasonable choice of $S(k_i)$ for the construction of a case-(2) distribution the corresponding effective dynamic polarizability will provide an upper bound to the actual dynamic polarizability. The distribution of Fig. 2 satisfies $S(-2)$ explicitly and bounds $S(-4)$,$S(-6),\ldots$ from above, so the effective dynamic polarizability corresponding to this distribution is seen to bound the actual dynamic polarizability from above. Identical arguments can be made to determine effective Verdet constants which bound the actual Verdet constants from above and below.

An important point is that these effective polarizabilities and Verdet constants provide a finite representation which bounds an expression which contains an infinite number of terms plus an integration over the continuum. Even though not exact, this representation seems to be an extremely useful way of writing these expressions. Including enough of the $S(-2)$, $S(-4)$, $S(-6),\ldots$ allows one to approach the exact function arbitrarily closely, not only by equaling the Cauchy series term by term for those $S(-2)$, $S(-4)$, $S(-6),\dots$ included explicitly, but by bounding those which are not included. Note that although this representation is valid only up to the first resonance, the frequency range may be extended by putting in actual physical states explicitly and using the method of effective modified oscillator-strength distributions. This functional form for the dynamic polarizability may prove to be a better finite representation to use for extracting $S(k)$ from experiment but this remains to be seen.

This discussion of bounds shall conclude with the subject of the C_6 coefficient in the van der Waals interaction. The reason for these bounds is subtler than the bounds described previously in this paper. For proofs the reader is referred to Langhoff and Karplus,[30] Langhoff, Gordon, and Karplus,[31] and Luyckx *et al.*[32] These bounds all require that the distributions be constructed from $S(k_i)$ with regularly spaced k_i. Here the sets of sums from which both upper and lower bounds on C_6 may be obtained will merely be listed. Lower bounds on C_6 may be obtained from

$$(S(2),S(1),S(0),S(-1),\dots)\ ,$$

$$(S(0),S(-1),S(-2),S(-3),\dots)\ ,$$

$$(S(-2)-,S(-3),S(-4),S(-5),\dots)\ ,$$

$$(S(-3),S(-4),S(-5),S(-6),\dots)\ ,$$

$$(S(-4),S(-5),S(-6),S(-7),\dots)\ ,$$

etc., and

$$(S(2),S(0),S(-2),S(-4),\dots)\ ,$$

$$(S(-2),S(-4),S(-6),S(-8),\dots)\ .$$

Upper bounds on C_6 may be obtained from

$$(S(1),S(0),S(-1),S(-2),\dots)\ ,$$

$$(S(-1),S(-2),S(-3),S(-4),\dots)\ ,$$

$$(S(0),S(-2),S(-4),S(-6),\dots)\ .$$

As usual, the C_6' is constructed by replacing the actual distributions in Eq. (6) by the effective distribution.

VII. CALCULATIONS FOR THE HYDROGEN ATOM

Fairly extensive calculations have been performed on the hydrogen atom because of the ready availability of exact values of $S(k_i)$ for $k_i=2,1,0,-1,-2,-3,\dots$. These $S(k)$ have been shown to be calculable in rational fraction form by Dalgarno and Kingston[33] who list $S(2),S(1),\dots,S(-6)$. Gavrila[34] has computed $S(-7),\dots,S(-10)$. Gavrila's value of $S(-10)$ contains a typographical error in the numerator which is listed correctly here. In addition $S(-11),\dots,S(-15)$ have been calculated in the present work in rational fraction form. All of these moments may be obtained by using recursion relations. The following list contains the previously calculated values of $S(k)$ along with the values of $S(-11),\dots,S(-15)$ calculated here:

$$S(2)=\tfrac{4}{3}\ ,$$

$$S(1)=\tfrac{2}{3}\ ,$$

$$S(0)=1\ ,$$

$$S(-1)=2\ ,$$

$$S(-2)=\tfrac{9}{2}\ ,$$

$$S(-3)=\tfrac{43}{4}\ ,$$

$$S(-4)=\tfrac{319}{12}\ ,$$

$$S(-5)=\tfrac{9673}{144}\ ,$$

$$S(-6)=\tfrac{297\,541}{1728}\ ,$$

$$S(-7)=\tfrac{9\,243\,157}{20\,736}\ ,$$

TABLE I. Partial listing of the polynomials used for the construction of effective oscillator-strength distributions for the ground state of atomic hydrogen. The roots of the polynomials give the energy differences between the ground state and the states of the effective oscillator-strength distribution (in a.u.).

$S(2)$:	$\frac{4}{9}(8\omega-3)$
$S(2)$—$S(1)$:	$\frac{2}{3}(\omega-2)$
$S(2)$—$S(0)$:	$[4/(27\times 13)](8\omega-3)(7\omega-26)$
$S(2)$—$S(-1)$:	$\frac{1}{9}(3\omega^2-18\omega+8)$
$S(2)$—$S(-2)$:	$[1/(2\times 9\times 107)](8\omega-3)(33\omega^2-306\omega+214)$
$S(2)$—$S(-3)$:	$[1/(2^2\times 9)](3\omega^3-36\omega^2+44\omega-12)$
$S(2)$—$S(-4)$:	$[1/(2^3\times 243\times 23)](8\omega-3)(75\omega^3-1260\omega^2+2180\omega-828)$
$S(2)$—$S(-5)$:	$[1/(2^6\times 27)](15\omega^4-300\omega^3+700\omega^2-476\omega+96)$
$S(1)$:	$\frac{2}{9}(8\omega-3)$
$S(1)$—$S(0)$:	$\frac{1}{3}(3\omega-2)$
$S(1)$—$S(-1)$:	$[1/(9\times 7)](8\omega-3)(6\omega-7)$
$S(1)$—$S(-2)$:	$[1/(2\times 3)](3\omega^2-6\omega+2)$
$S(1)$—$S(-3)$:	$[1/(2^3\times 9\times 11)](8\omega-3)(15\omega^2-45\omega+22)$
$S(1)$—$S(-4)$:	$[1/(2^4\times 9)](15\omega^3-60\omega^2+52\omega-12)$
$S(1)$—$S(-5)$:	$[1/(2^8\times 81)](8\omega-3)(30\omega^3-165\omega^2+194\omega-60)$
$S(1)$—$S(-6)$:	$[5/(2^{10}\times 27)](45\omega^4-300\omega^3+480\omega^2-268\omega+48)$

$$S(-8)=\frac{289\,165\,453}{248\,832}\,,$$

$$S(-9)=\frac{45\,464\,213\,273}{14\,929\,920}\,,$$

$$S(-10)=\frac{7\,175\,468\,425\,141}{895\,795\,200}\,,$$

$$S(-11)=\frac{1\,135\,753\,416\,866\,657}{53\,747\,712\,000}\,,$$

$$S(-12)=\frac{180\,168\,229\,948\,381\,789}{3\,224\,862\,720\,000}\,,$$

$$S(-13)=\frac{200\,407\,807\,104\,309\,615\,071}{1\,354\,442\,342\,400\,000}\,,$$

$$S(-14)=\frac{223\,220\,093\,886\,359\,508\,924\,469}{568\,865\,783\,808\,000\,000}\,,$$

$$S(-15)=\frac{248\,892\,118\,198\,506\,334\,751\,975\,591}{238\,923\,629\,199\,360\,000\,000}\,.$$

In addition, values of the following sums have been computed, valid to 25 digits:

$$S(-16)=2.767\,867\,752\,796\,214\,680\,257\,191\times10^{6}\,,$$

$$S(-17)=7.359\,191\,237\,809\,297\,517\,598\,849\times10^{6}\,,$$

$$S(-18)=1.957\,712\,849\,836\,060\,068\,184\,363\times10^{7}\,.$$

For the construction of the case-(2) distributions it is also necessary to know that $\omega_1=\frac{3}{8}$ a.u.

Using this collection of sums Prony's method has been implemented to set up the polynomial equation (for the effective energy differences) with rational coefficients for both case-(1) and case-(2) distributions. Calculations have been performed including sums from $S(2)$ and $S(1)$ ranging over values down to $S(-17)$ and $S(-18)$. Table I contains a partial listing of the polynomials used for the construction of the effective distributions. A complete listing of the polynomials may be found in Ref. 13.

The roots of these polynomials were evaluated using the Newton-Raphson method. After the effective energy differences were obtained, the effective oscillator strengths were calculated using the previously described technique which utilized the alternant form of the matrix for inversion. Once the effective oscillator strengths and energy differences were known, the distribution was inserted into the various second-order perturbation expressions. All calculations have been performed to double precision (28 digits). In all cases the effective distributions were found to satisfy the constraint (i.e., initial) $S(k_i)$ to at least 20 digits.

The case-(1) distributions which satisfy the criteria set forth by Luyckx *et al.*[32] can be used to obtain both upper and lower bounds on the C_6 coefficient. Table II lists the

TABLE II. Values of the van der Waals coefficient calculated using effective distributions.

Sums included	C_6
$S(2)$–$S(1)$	0.010 416 666 7
$S(2)$–$(S-1)$	6.171 875 000 0
$S(2)$–$S(-3)$	6.486 918 604 7
$S(2)$–$S(-5)$	6.498 585 838 5
$S(2)$–$S(-7)$	6.499 007 944 0
$S(2)$–$S(-9)$	6.499 025 644 9
$S(2)$–$S(-11)$	6.499 026 619 6
$S(2)$–$S(-13)$	6.499 026 695 7
$S(2)$–$S(-15)$	6.499 026 704 0
$S(2)$–$S(-17)$	6.499 026 705 1
$S(1)$–$S(0)$	2.531 250 000 0
$S(1)$–$S(-2)$	6.562 500 000 0
$S(1)$–$S(-4)$	6.501 275 510 2
$S(1)$–$S(-6)$	6.499 114 205 2
$S(1)$–$S(-8)$	6.499 030 949 3
$S(1)$–$S(-10)$	6.499 026 992 1
$S(1)$–$S(-12)$	6.499 026 733 1
$S(1)$–$S(-14)$	6.499 026 709 1
$S(1)$–$S(-16)$	6.499 026 706 0
$S(1)$–$S(-18)$	6.499 026 705 5

TABLE III. Values of the logarithmic mean excitation energies calculated using effective distribution.

Sums included	$L(-1)$	$L(0)$	$L(1)$	$L(2)$
$S(2)$–$S(1)$	0.115 524 5	0.462 10	1.848	7.39
$S(2)$–$S(0)$	−0.326 494 6	−0.087 40	1.104	9.52
$S(2)$–$S(-1)$	−0.025 752 0	0.054 86	0.933	10.61
$S(2)$–$S(-2)$	−0.068 119 1	0.085 74	0.846	11.59
$S(2)$–$S(-3)$	−0.071 582 8	0.091 34	0.820	12.03
$S(2)$–$S(-4)$	−0.072 848 2	0.094 78	0.796	12.60
$S(2)$–$S(-5)$	−0.073 049 1	0.095 57	0.788	12.85
$S(2)$–$S(-6)$	−0.073 184 8	0.096 31	0.779	13.23
$S(2)$–$S(-7)$	−0.073 211 6	0.096 50	0.776	13.38
$S(2)$–$S(-8)$	−0.073 236 5	0.096 72	0.771	13.65
$S(2)$–$S(-9)$	−0.073 242 0	0.096 78	0.770	13.75
$S(2)$–$S(-10)$	−0.073 248 2	0.096 86	0.768	13.95
$S(2)$–$S(-11)$	−0.073 249 7	0.096 89	0.767	14.03
$S(2)$–$S(-12)$	−0.073 251 7	0.096 92	0.766	14.18
$S(2)$–$S(-13)$	−0.073 252 2	0.096 93	0.765	14.24
$S(2)$–$S(-14)$	−0.073 252 9	0.096 95	0.764	14.37
$S(2)$–$S(-15)$	−0.073 253 1	0.096 95	0.764	14.41
$S(2)$–$S(-16)$	−0.073 253 3	0.096 96	0.763	14.51
$S(2)$–$S(-17)$	−0.073 253 4	0.096 96	0.763	14.55
Actual	−0.073 253 8	0.096 98	0.761	15.92

TABLE IV. Values of the logarithmic mean excitation energies calculated using effective distributions.

Sums included	$L(-1)$	$L(0)$	$L(1)$	$L(2)$
$S(1)$—$S(0)$	0.215 767 1	0.287 68	0.384	0.51
$S(1)$—$S(-1)$	−0.108 474 7	0.130 47	0.592	1.60
$S(1)$—$S(-2)$	−0.079 844 9	0.110 24	0.654	2.32
$S(1)$—$S(-3)$	−0.074 466 6	0.101 50	0.701	3.35
$S(1)$—$S(-4)$	−0.073 774 0	0.099 62	0.716	3.87
$S(1)$—$S(-5)$	−0.073 407 0	0.098 15	0.732	4.73
$S(1)$—$S(-6)$	−0.073 340 4	0.097 78	0.738	5.12
$S(1)$—$S(-7)$	−0.073 286 4	0.097 39	0.745	5.82
$S(1)$—$S(-8)$	−0.073 275 0	0.097 29	0.747	6.12
$S(1)$—$S(-9)$	−0.073 263 1	0.097 16	0.751	6.71
$S(1)$—$S(-10)$	−0.073 260 4	0.097 12	0.752	6.95
$S(1)$—$S(-11)$	−0.073 257 0	0.097 07	0.755	7.44
$S(1)$—$S(-12)$	−0.073 256 2	0.097 05	0.755	7.64
$S(1)$—$S(-13)$	−0.073 255 1	0.097 03	0.757	8.06
$S(1)$—$S(-14)$	−0.073 254 8	0.097 02	0.757	8.22
$S(1)$—$S(-15)$	−0.073 254 4	0.097 01	0.758	8.58
$S(1)$—$S(-16)$	−0.073 254 2	0.097 00	0.758	8.72
$S(1)$—$S(-17)$	−0.073 254 0	0.097 00	0.759	9.03
$S(1)$—$S(-18)$	−0.073 254 0	0.097 00	0.759	9.15
Actual	−0.073 253 8	0.096 98	0.761	15.92

values of C_6 obtained from the effective distributions. All values obtained from the $S(2)$—$S(3-2N)$ distributions and the $S(1)$—$S(0)$ distribution are guaranteed to provide a lower bound to C_6. All values obtained from the $S(1)$—$S(2-2N)$ distributions with the exception of the $S(1)$—$S(0)$ distribution, are guaranteed to provide an upper bound to C_6. Deal[35] has calculated C_6 to 11 digits as 6.499 026 705 4. The values obtained here bound this result from above and below as claimed.

The case-(1) and case-(2) distributions can be used to compute upper and lower bounds on the logarithmic sums $L(k_i)$ as described earlier. Results from the effective distributions are presented in Tables III and IV. The actual values have been taken from Shimamura.[36] The bounding behavior is seen to be in accordance with that described previously. As far as the accuracy of this technique is concerned, the results are good for $L(-1)$ and $L(0)$, fair for $L(1)$, and not encouraging for $L(2)$.

It should be noted that the variational perturbation basis of Johnson, Epstein, and Meath[37] yields an effective oscillator-strength distribution which satisfies $S(0)$, $S(-1)$, $S(-2)$, $S(-3)$, ... But the variational perturbation technique does not have the flexibility of the method described here and it cannot be used to obtain all the bounds on C_6 and the logarithmic sums.

VIII. CONCLUSION

It has been shown that Prony's method of exponential interpolation provides a simple method for solving the equations required for the construction of effective oscillator-strength distributions. Using Prony's method also leads to a new closed-form expression for an upper bound to the static polarizability in terms of $S(-1)$, $S(0)$, $S(1)$, and ω_1. The calculations of effective oscillator-strength distributions of the ground state of atomic hydrogen have led to bounds on logarithmic mean excitation energies and C_6 which are in accordance with the bounding behavior discussed in Sec. VI.

ACKNOWLEDGMENTS

I would like to thank Professor J. C. Browne for advice and encouragement throughout this work. I am grateful to Dr. E. J. Shipsey for many useful discussions concerning the work. This research was supported by the Robert A. Welch Foundation of Houston, Texas under Grant No. F-379.

---

[1] R. G. Gordon, J. Chem. Phys. **48**, 3929 (1968).

[2] R. De Prony, J. Ec. Polytech. **1** (2), 24 (1775).

[3] U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).

[4] J. O. Hirschfelder, W. Byers-Brown, and S. T. Epstein, Adv. Quantum Chem. **1**, 256 (1964).

[5] I. Shimamura and M. Inokuti, Phys. Rev. A **23**, 2914 (1981).

[6] M. Inokuti, Y. Kim, and R. L. Platzman, Phys. Rev. **164**, 55 (1967).

[7] H. A. Bethe, Ann. Phys. (Leipzig) **5**, 325 (1930).

[8] U. Fano, Annu. Rev. Nucl. Sci. **13**, 1 (1963).

[9] H. A. Bethe, Phys. Rev. **72**, 339 (1947).

[10] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Plenum, New York, 1977).

[11] R. Jackiw, Phys. Rev. **157**, 1220 (1967).

[12] M. C. Struensee, Phys. Rev. A **30**, 2339 (1984).

[13] M. C. Struensee, Ph.D. thesis, University of Texas at Austin, 1984.

[14] P. W. Langhoff and M. Karplus, J. Opt. Soc. Am. **59**, 863 (1969).

[15] R. G. Gordon, J. Math. Phys. **9**, 655 (1968).

[16] J. C. Wheeler and R. G. Gordon, in *The Padé Approximant in Theoretical Physics,* edited by G. A. Baker and J. L. Gammel

(Academic, New York, 1970).
[17] R. Luyckx, Ph. Coulon, and H. N. W. Lekkerkerker, J. Chem. Phys. **71**, 4734 (1979).
[18] E. T. Whittaker and G. Robinson, *The Calculus of Observations* (Dover, New York, 1967).
[19] A. C. Aitken, *Determinants and Matrices* (Oliver and Boyd, Edinburgh, 1956).
[20] R. P. Futrelle and D. A. McQuarrie, Chem. Phys. Lett. **2**, 223 (1968).
[21] J. G. Kirkwood, Phys. Z. (Leipzig) **33**, 57 (1932).
[22] J. P. Vinti, Phys. Rev. **41**, 813 (1932).
[23] F. Weinhold, J. Phys. A **1**, 655 (1968).
[24] C. L. Pekeris, Phys. Rev. **115**, 1216 (1959).
[25] C. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1949).
[26] R. M. Glover and F. Weinhold, J. Chem. Phys. **65**, 4913 (1976).
[27] B. Schiff and C. L. Pekeris, Phys. Rev. **134**, A638 (1964).
[28] P. W. Langhoff and A. C. Yates, J. Phys. B **5**, 1071 (1972).
[29] M. Barnsley, J. Math. Phys. **12**, 957 (1971).
[30] P. W. Langhoff and M. Karplus, in *The Padé Approximant in Theoretical Physics,* edited by G. A. Baker and J. L. Gammel (Academic, New York, 1970).
[31] P. W. Langhoff, R. G. Gordon, and M. Karplus, J. Chem. Phys. **55**, 2126 (1971).
[32] R. Luyckx, F. Delbaen, Ph. Coulon, and H. N. W. Lekkerkerker, Phys. Rev. A **19**, 324 (1979).
[33] A. Dalgarno and A. E. Kingston, Proc. R. Soc. London, Ser. A **259**, 424 (1960).
[34] M. Gavrila, Phys. Rev. **163**, 147 (1967).
[35] W. Deal, Int. J. Quantum Chem. **6**, 593 (1972).
[36] I. Shimamura, J. Phys. Soc. Jpn. **40**, 239 (1976).
[37] R. E. Johnson, S. T. Epstein, and W. J. Meath, J. Chem. Phys. **41**, 3955 (1964).