USES OF DIPOLE OSCILLATOR STRENGTH SUM RULES
IN SECOND ORDER PERTURBATION THEORY

Michael Calvin Struensee

Department of Computer Sciences
University of Texas at Austin
Austin, Texas 78712

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by

Michael Calvin Struensee, B.A.

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Michael Calvin Struensee, Ph.D.
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Supervising Professor: James C. Browne

Certain moments of the dipole oscillator strength distribution of atoms and molecules can be calculated from theory (using "sum rules") or deduced from experiment. The present work describes the use of these moments to construct effective distributions which lead to bounds and estimates of physical properties of interest. Asymptotic analysis is then used to obtain the high energy behavior of the oscillator strength density and a previously unknown sum rule for atoms and molecules. A new type of effective distribution, which incorporates the information concerning the asymptotic behavior and the new sum rule, is suggested. This new type of distribution is used to calculate the logarithmic mean excitation energies for the ground states of atomic hydrogen, atomic helium and the negative hydrogen ion. The calculations for atomic helium and the negative hydrogen ion require the evaluation of certain ground state expectation values. These have been calculated using high accuracy wavefunctions containing the nonconventional terms shown by Fock to be necessary for a correct analytic expansion when both electrons are near the nucleus.

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CHAPTER I

INTRODUCTION

Nondegenerate perturbation theory is a useful technique for evaluating properties of atoms and molecules. First order perturbation quantities associated with a state may be evaluated if the corresponding wavefunction is known. However, evaluation of second and higher order perturbation quantities requires knowledge of the entire spectrum of states of the unperturbed Hamiltonian. With the exception of simple systems such as atomic hydrogen, it is impossible to obtain the complete set of states required to perform the evaluation.

The present work deals primarily with the evaluation of second order perturbation expressions which require the knowledge of the dipole oscillator strength between the state of interest and all other states of the system. These expressions arise for properties characterizing interactions of atoms and molecules with static electric fields, electromagnetic radiation and fast charged particles. Examples of the properties under consideration here are the static and dynamic polarizability, the coefficient of the $1/R^6$ term in the Van der Waals interaction energy, the Verdet constant, and the logarithmic mean excitation energies, all described in Chapter II.

The second order perturbation expressions under consideration here can be evaluated if the dipole oscillator strength distribution is known. This is equivalent to knowing the entire spectrum of states (more precisely, those allowed by selection rules) and is, of course, impossible to achieve except for simple systems such as atomic hydrogen. However, certain moments (with respect to the energy) of the oscillator strength distribution can be calculated in terms of ground state expectation values. Other moments of the distribution can be deduced from experiment or calculated vari-

ationally. Chapter II discusses how a set of accurate moments of the distribution can be used to determine upper and lower bounds on the properties under consideration. The method requires the solution to a system of nonlinear algebraic equations and a new technique for obtaining this solution is presented here. Extensive calculations have been performed for atomic hydrogen.

Chapter III contains a discussion of the generalization of the definition of the dipole oscillator strength to electric multipole operators and a definition of multipole oscillator strengths is developed. Applications of multipole oscillator strengths to static electric field problems and radiation problems are then presented. A procedure for performing variational calculations of the moments of the dipole oscillator strength distribution is then described, which is easily extended to deal with the multipole case. Variational calculations of the logarithmic mean excitation energies are discussed and extensive calculations have been performed for the hydrogen atom. These calculations generated an effective set of states which has also been used to evaluate C_6, the coefficient of the $1/R^6$ term in the Van der Waals interaction energy. The result has converged to 18 digits, apparently the most accurate calculation to date. Finally, applications of variational calculations to the evaluation of the low energy photoionization cross section is discussed and results are presented for atomic hydrogen.

Chapter IV contains a discussion of the high energy asymptotic behavior of the oscillator strength distribution of N-electron atoms and molecules. A derivation is presented which leads to the coefficients of the first two asymptotic terms of the oscillator strength density in terms of expectation values of the wavefunction. Furthermore it is shown that truncating the contribution of these first two terms beyond some cut off energy leads to a sum rule for the third moment of the resulting modified distribution. None of these results have previously been known.

Chapter V uses the results derived in Chapter IV to provide a more efficient method of computing the logarithmic mean excitation

energies and the high energy photoionization cross section. This technique is then applied to atomic hydrogen with very encouraging results.

Finally, the method described in Chapter V is utilized in Chapter VI to compute the logarithmic mean excitation energies of the ground state of atomic helium and the negative hydrogen ion. Various values required for the calculation were taken from the literature, however certain ground state expectation values were not available. In order to evaluate these expectation values, calculations were performed using a Fock type wavefunction with up to 162 terms. Results are also presented which allow the calculation of the high energy photoionization cross section for the ground state of atomic helium and the negative hydrogen ion.

CHAPTER II

USES OF DIPOLE OSCILLATOR STRENGTH SUMS IN PERTURBATION THEORY

A. 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. For higher order multipole interactions, quadrupole matrix elements, octupole matrix elements, etc. appear in the expressions, but here only the dipole case will be considered. 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 states are possible only for low lying bound states which by themselves are not sufficient to allow evaluation of the perturbation expressions. However more will be said about variational techniques for generating useful "approximate" oscillator strength distributions in Chapter III.

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.

B. 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 dynamic polarizability tensor for a state $|n\rangle$ is defined[5] to be

$$\alpha_{ij}^{(n)}(\omega) = 2 \sum_b \frac{\langle n| \sum_\mu r_{i\mu}|b\rangle \langle b| \sum_\nu r_{j\nu}|n\rangle (E_b - E_n)}{(E_b - E_n)^2 - \omega^2} \tag{1}$$

where b ranges over all states such that $E_b \neq E_n$, μ and ν range over all electrons of the atom or molecule, and $r_{1\mu} = x_\mu$, $r_{2\mu} = y_\mu$, and $r_{3\mu} = z_\mu$. The "damping term" sometimes included in the denominator and associated with the natural width of the spectral lines has been neglected. Here, and throughout the remainder of this work unless mentioned otherwise, the energies shall be taken in atomic units (i.e. twice the ionization potential of atomic hydrogen) and the frequencies shall be taken in units of twice the Rydberg frequency (i.e. twice the ionization frequency of atomic hydrogen). The polarizability is expressed in units of the cube of the Bohr radius of the hydrogen atom ($\hbar^2/(e^2 m)$). The average polarizability is then given by

$$\alpha^{(n)}(\omega) = \frac{1}{3} \left(\alpha_{11}^{(n)} + \alpha_{22}^{(n)} + \alpha_{33}^{(n)} \right) . \tag{2}$$

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

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

where $\omega_{nb} = E_b - E_n$. Therefore the average polarizability may be written

$$\alpha^{(n)}(\omega) = \sum_b \frac{f_{nb}}{\omega_{nb}^2 - \omega^2} . \tag{4}$$

For the following discussion $|n\rangle$ will be taken to be $|0\rangle$, the ground state and $\alpha^{(0)}(\omega)$ will be denoted by $\alpha(\omega)$. The dipole oscillator strength sum of order k is defined by

$$S(k) = \sum_b f_{ob} \left(\omega_{ob} \right)^k \tag{5}$$

where f_{0b} and ω_{0b} are the oscillator strengths and energy differences between the ground state and the excited states.

The dynamic polarizability may be written as a power series in ω using S(k). This is known as the Cauchy expansion[6-8] and converges for ω less than the first transition frequency. The derivation is quite straightforward:

$$\alpha(\omega) = \sum_b \frac{f_{ob}}{\omega_{ob}^2 - \omega^2}$$

$$= \sum_b \frac{f_{ob}}{\omega_{ob}^2 \left(1 - \frac{\omega^2}{\omega_{ob}^2}\right)}$$

$$= \sum_b \frac{f_{ob}}{\omega_{ob}^2} \left(1 + \frac{\omega^2}{\omega_{ob}^2} + \frac{\omega^4}{\omega_{ob}^4} + \cdots\right)$$

$$= S(-2) + S(-4)\omega^2 + S(-6)\omega^4 + \cdots . \tag{6}$$

The dynamic polarizability is required for calculations involving the elastic scattering of light by atoms and molecules[9-12]. Knowing the dynamic polarizability allows the evaluation of the Rayleigh scattering cross section $\frac{d\sigma}{d\Omega}(\omega)$ which is obtained by averaging over all polarizations of the light and orientations of the atom or molecule,

$$\frac{d\sigma}{d\Omega}(\omega) = \frac{r_o^2}{2} \left(1 + \cos^2\theta\right) \left[\omega^2 \alpha(\omega)\right]^2 \tag{7}$$

where θ is measured from the direction of propagation of the light, and $r_0 = e^2/(mc^2)$ is the classical electron radius. The polarizability is also needed to determine the index of refraction[8]. The index of refraction, n, satisfies the Lorentz-Lorenz equation

$$n^2 - 1 = \frac{4\pi}{3} \left(n^2 + 2\right) N \alpha(\omega) \tag{8}$$

where N is the number of atoms or molecules per unit volume. If the medium is a dilute gas then n will be close to unity, hence the Lorentz factor $(n^2 + 2)/3$ will also be close to unity. The equation then becomes

$$n^2 - 1 = 4\pi N \alpha(\omega) . \tag{9}$$

Knowledge of the oscillator strength distribution also allows the evaluation of the Verdet constant, which characterizes the Faraday effect[10,13,14]. The Faraday effect consists of the rotation of plane polarized light passing through a medium in a magnetic field. The rotation is a result of the difference in the index of refraction of right and left-hand circularly polarized light. The Verdet constant is proportional to $\beta(\omega)$ where

$$\beta(\omega) = \sum_b \frac{f_{ob}\,\omega^2}{(\omega_{ob}^2 - \omega^2)^2} . \tag{10}$$

This is clearly related to $\alpha(\omega)$ by

$$\beta(\omega) = \frac{1}{2}\,\omega\,\frac{d\alpha(\omega)}{d\omega} \tag{11}$$

and a "Cauchy expansion" for $\beta(\omega)$ yields

$$\beta(\omega) = S(-4)\,\omega^2 + 2\,S(-6)\,\omega^4 + 3\,S(-8)\,\omega^6 + \cdots . \tag{12}$$

The coefficient $C_{\gamma\delta}$ of the $1/R^6$ term in the Van der Waals interaction energy between two ground state atoms γ and δ is due to a dipole-dipole interaction. Using second order perturbation theory it is found[4] that

$$C_{\gamma\delta} = \frac{3}{2} \sum_m \sum_n \frac{f_{om}(\gamma)\,f_{on}(\delta)}{[\omega_{om}(\gamma) + \omega_{on}(\delta)]\,\omega_{om}(\gamma)\,\omega_{on}(\delta)} . \tag{13}$$

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

The logarithmic mean excitation energies are defined[15] by

$$L(k) = \sum_b f_{ob}\,(\omega_{ob})^k\,\ln(\omega_{ob}) . \tag{14}$$

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 section - Inokuti, et.al.[16], 1967.

    b. L(0) - For stopping power (mean energy loss) - Bethe[17], 1930.

    c. L(1) - For straggling(mean fluctuation of energy loss) - Fano[18], 1963.

2. L(2) - For the Lamb shift - Bethe[19], 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 equations (5) and (14) that L(k) is merely the slope of S(k), i.e.

$$L(k) = \frac{d}{dx} S(x) \bigg|_{x=k} \quad . \tag{15}$$

C. 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 wavefunction 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, -8, ... respectively.

The well known "sum rules"[3,20] express S(2), S(1), S(0) and S(-1) in terms of expectation values of the wavefunction. Given an accurate wavefunction, these sums may be readily computed. For a state $|\psi\rangle$ the S(k) can be written as

$$S(2) = \frac{4\pi}{3} \sum_{\alpha} Z_{\alpha} \left\langle \psi \bigg| \sum_{j=1}^{N} \delta(\vec{r}_{j\alpha}) \bigg| \psi \right\rangle \tag{16}$$

$$S(1) = \frac{2}{3} \langle \Psi | (\sum_{j=1}^{N} \vec{p}_j)^2 | \Psi \rangle \tag{17}$$

$$S(0) = N \tag{18}$$

$$S(-1) = \frac{2}{3} \langle \Psi | (\sum_{j=1}^{N} \vec{r}_j)^2 | \Psi \rangle \tag{19}$$

where $\vec{r}_j$ is the position operator, $\vec{p}_j$ 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[21], but are not useful for atomic and molecular ground states because S(k) diverges at k = 2.5 for these wavefunctions. 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 non-vanishing 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 asymptotic form of $df/d\epsilon$ for any atomic wavefunction (as will be proven in Chapter IV) is

$$\frac{df}{d\epsilon} = \frac{2\sqrt{2} \, Z}{\pi} S(2) \epsilon^{-3.5} - 2 Z^2 S(2) \epsilon^{-4} + \cdots . \tag{20}$$

Clearly if S(2) ≠ 0 then the continuum integration contribution to S(k),

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

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 compute 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. Hirschfelder, Byers-Brown and Epstein[4] note that S(-3) is twice the norm of the first order perturbation wavefunction for a dipole interaction. This would seem to indicate that if an accurate value of S(-2) is obtained using a variational basis, the same basis should yield a good value for S(-3). Further discussion of variational techniques for obtaining S(k) shall be deferred to Chapter III. Note that the method to be described of constructing effective distributions is capable of yielding exact bounds on perturbation expressions only if given an exact set of S(k). Therefore, additional S(k) are useful only if they are accurate.

Ab initio techniques are questionable for obtaining accurate S(k) for $k < -3$, but fortunately it is possible to obtain certain S(k) in this range from experiment. As described above, the dynamic polarizability and the Verdet constant may be written as a Cauchy expansion in terms of S(k) with k ranging over even negative integers. For a dilute gas the index of refraction, n, will be close to unity, hence equation (9) may be approximated by

$$n(\omega) = 1 + 2\pi N \alpha(\omega) . \tag{21}$$

Substituting the Cauchy series expansion (6) for $\alpha(\omega)$ yields

$$n(\omega) = 1 + 2\pi N [S(-2) + S(-4)\omega^2 + S(-6)\omega^4 + \cdots] . \tag{22}$$

The standard method of utilizing this equation is to truncate the series on the right hand side and keep terms only up to ω^6 or ω^8. Then a polynomial least squares fit is performed to extract S(-2), S(-4), and S(-6), using experimental values of $n(\omega)$ over a range of ω (such that ω is appreciably less than the first transition frequency). For details see Langhoff and Karplus[22]. A similar procedure may be followed for the Verdet constant using the Cauchy expan-

sion for $\beta(\omega)$ given by equation (12).

D. 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 wavefunction 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, ..., 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.

$$S_m(k) = S(k) - \sum_{\substack{a \\ E_a < E_n}} f_{na} \, \omega_{na}^k \; . \tag{23}$$

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, ..., 2N. The effective distribution f'_b, ω'_b, b = 1, 2, ..., N, is determined by the system of equations

$$S(k_i) = \sum_{b=1}^{N} f'_b \left(\omega'_b \right)^{k_i} \qquad i = 1, 2, \cdots, 2N \; . \tag{24}$$

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

$$S(k_i) = \sum_{b=1}^{N} f_b' \, (\omega_b')^{k_i} \qquad i = 1, 2, \cdots, 2N-1 \qquad (25)$$

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 (24) or (25). 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[23] managed to turn the problem of solving case 1) into one of diagonalizing a tridiagonal matrix with entries constructed from the $S(k_i)$ by using recursion relations from the theory of continued fractions. Another description of this technique is found in Wheeler and Gordon[24]. Luyckx, et.al.[25] formulate case 1) in terms of an eigenvalue problem without the need for continued fraction recursion relations. Shimamura and Inokuti[15] 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 exponen-

tial 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[26], Prony's method of exponential interpolation shall be explained in terms of case 1). Recall the system of equations which must be solved is

$$S(k_1) = \sum_{b=1}^{N} f_b' \left(\omega_b'\right)^{k_1}$$

$$S(k_2) = \sum_{b=1}^{N} f_b' \left(\omega_b'\right)^{k_2} \tag{24'}$$

$$\vdots$$

$$S(k_{2N}) = \sum_{b=1}^{N} f_b' \left(\omega_b'\right)^{k_{2N}} .$$

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

$$S'(k) = \sum_{b=1}^{N} f_b' \left(\omega_b'\right)^{k} \tag{26}$$

which satisfies the equations

$$S'(k_i) = S(k_i) \qquad i = 1, 2, \cdots, 2N . \tag{27}$$

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

$$S'(k+i) = \sum_{b=1}^{N} \left[f_b' \left(\omega_b' \right)^i \right] \left(\omega_b' \right)^k$$

hence

$$F_i(k) = \sum_{b=1}^{N} c_{ib} \, G_b(k) \tag{26'}$$

where

$$F_i(k) = S'(k+i)$$

$$G_b(k) = \left(\omega_b' \right)^k$$

$$c_{ib} = f_b' \left(\omega_b' \right)^i .$$

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 equation (26') is indeed nonsingular, i.e. the determinant is nonzero.

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

$$= f_1 f_2 \cdots f_N \, \omega_1 \omega_2 \cdots \omega_N \begin{vmatrix} 1 & 1 & \cdot & \cdot & \cdot & 1 \\ \omega_1 & \omega_2 & \cdot & \cdot & \cdot & \omega_N \\ \vdots & \vdots & & & & \\ \omega_1^{N-1} & \omega_2^{N-1} & \cdot & \cdot & \cdot & \omega_N^{N-1} \end{vmatrix}$$

$$= f_1 f_2 \cdots f_N \, \omega_1 \omega_2 \cdots \omega_N \times$$
$$\times (\omega_N - \omega_{N-1}) \times (\omega_N - \omega_{N-2}) \times \cdots \times (\omega_N - \omega_1) \times$$
$$\times (\omega_{N-1} - \omega_{N-2}) \times (\omega_{N-1} - \omega_{N-3}) \times \cdots \times (\omega_{N-1} - \omega_1) \times$$
$$\times \cdots \times$$
$$\times (\omega_2 - \omega_1)$$

where the last step has been performed by the difference-product expansion of the alternant determinant[27]. 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, ..., 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 $F_0(k)$, $F_1(k)$, ..., $F_N(k)$ must clearly be linearly dependent. Therefore there exist unique (up to an overall scale) α_j such that

$$\alpha_0 F_0(k) + \alpha_1 F_1(k) + \cdots + \alpha_N F_N(k) = 0$$

or equivalently

$$\alpha_0 S'(k) + \alpha_1 S'(k+1) + \cdots + \alpha_N S'(k+N) = 0 . \tag{28}$$

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

rewritten

$$\alpha_o \sum_{b=1}^{N} f_b'(\omega_b')^k + \alpha_1 \sum_{b=1}^{N} f_b'(\omega_b')^{k+1} + \cdots + \alpha_N \sum_{b=1}^{N} f_b'(\omega_b')^{k+N} = 0 \qquad (29)$$

or

$$\sum_{b=1}^{N} \left[\alpha_N (\omega_b')^N + \alpha_{N-1}(\omega_b')^{N-1} + \cdots + \alpha_o \right] f_b'(\omega_b')^k = 0 . \qquad (29')$$

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

$$\alpha_N (\omega_b')^N + \alpha_{N-1}(\omega_b')^{N-1} + \cdots + \alpha_o = 0 . \qquad (30)$$

Therefore once the α_j have been found all that remains is to determine the roots of equation (30) in order to obtain the N effective energy differences ω_b'. The α_j may be determined using equation (28) in conjunction with the known $S(k_i)$ where $k_i = k_0 + i$, $i = 1, 2, \ldots,$ 2N (recall it was assumed that the $S(k_i)$ were known for integrally spaced k_i). Utilizing equation (28) N simultaneous equations are constructed by replacing k with k_0+1, k_0+2, $\ldots$, k_0+N. Doing this yields the system

$$\alpha_o S'(k_o+1) + \alpha_1 S'(k_o+2) + \cdots + \alpha_N S'(k_o+N+1) = 0$$

$$\alpha_o S'(k_o+2) + \alpha_1 S'(k_o+3) + \cdots + \alpha_N S'(k_o+N+2) = 0$$

$$\vdots \qquad \vdots \qquad \qquad \vdots \qquad \vdots \qquad (31)$$

$$\alpha_o S'(k_o+N) + \alpha_1 S'(k_o+N+1) + \cdots + \alpha_N S'(k_o+2N) = 0 .$$

From equation (27) it follows that for the arguments of $S(k)$ in the above equations $S'(k) = S(k)$ so equation (31) may be rewritten as

$$\alpha_0 S(k_0+1) + \alpha_1 S(k_0+2) + \cdots + \alpha_N S(k_0+N+1) = 0$$

$$\alpha_0 S(k_0+2) + \alpha_1 S(k_0+3) + \cdots + \alpha_N S(k_0+N+2) = 0$$

$$\vdots \qquad\qquad \vdots \qquad\qquad\qquad \vdots \qquad\qquad \vdots \tag{32}$$

$$\alpha_0 S(k_0+N) + \alpha_1 S(k_0+N+1) + \cdots + \alpha_N S(k_0+2N) = 0$$

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 so a solution can be easily obtained for the system which is unique up to an overall scale. Using Cramer's rule[27], one way of writing the solution is the following:

$$\alpha_N = \begin{vmatrix} S(k_0+1) & S(k_0+2) & \ldots & S(k_0+N) \\ S(k_0+2) & S(k_0+3) & \ldots & S(k_0+N+1) \\ \vdots & \vdots & & \vdots \\ S(k_0+N) & S(k_0+N+1) & \ldots & S(k_0+2N-1) \end{vmatrix} \tag{33}$$

$$\alpha_{N-1} = - \begin{vmatrix} S(k_0+1) & S(k_0+2) & \ldots & S(k_0+N) \\ S(k_0+2) & S(k_0+3) & \ldots & S(k_0+N+1) \\ \vdots & \vdots & & \vdots \\ S(k_0+N-2) & S(k_0+N-1) & \ldots & S(k_0+2N-3) \\ S(k_0+N-1) & S(k_0+N) & \ldots & S(k_0+2N-2) \\ S(k_0+N+1) & S(k_0+N+2) & \ldots & S(k_0+2N) \end{vmatrix} \tag{34}$$

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):

$$
\begin{array}{llll}
\text{0th row:} & S(k_0+1) & S(k_0+2) & \ldots & S(k_0+N) \\
\text{1st row:} & S(k_0+2) & S(k_0+3) & \ldots & S(k_0+N+1) \\
\text{2nd row:} & S(k_0+3) & S(k_0+4) & \ldots & S(k_0+N+2) \\
& \vdots & \vdots & & \vdots \\
\text{Nth row:} & S(k_0+N+1) & S(k_0+N+2) & \ldots & S(k_0+2N) \ .
\end{array}
\tag{35}
$$

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, $j = 1, 2, \ldots, N$. 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:

$$
\begin{vmatrix}
1 & S(k_0+1) & S(k_0+2) & \ldots & S(k_0+N) \\
\omega' & S(k_0+2) & S(k_0+3) & \ldots & S(k_0+N+1) \\
\omega'^2 & S(k_0+3) & S(k_0+4) & \ldots & S(k_0+N+2) \\
\vdots & \vdots & \vdots & & \vdots \\
\omega'^N & S(k_0+N+1) & S(k_0+N+2) & \ldots & S(k_0+2N)
\end{vmatrix}
= 0
\tag{36}
$$

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 equation (35):

$$\begin{pmatrix} S(-3) & S(-2) & S(-1) \\ S(-2) & S(-1) & S(0) \\ S(-1) & S(0) & S(1) \\ S(0) & S(1) & S(2) \end{pmatrix}$$

Using the above procedure the effective energies are obtained by solving

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

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

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

The matrix that must be inverted is known as an alternant matrix and closed form inversion is especially simple[27].

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

$$
S'(-2) = \frac{S(-1)(\omega_1^2 S(-1) - S(1)) - S(0)(\omega_1 S(-1) - S(0))}{\omega_1(\omega_1 S(0) - S(1))} \tag{37}
$$

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.

E. 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 equation (37) 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 (37) 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 equation (37) provides a useful bound on the static polarizability.

The reason for the bounding behavior of equation (37) will be deferred until the next section, 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[28], 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

   a. $S'_{1a}(-2) = \dfrac{(S(-1))^2}{S(0)}$.

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

2. Upper bounds

   a. $S'_{2a}(-2) = \dfrac{S(-1)}{\omega_1}$.

   b. $S'_{2b}(-2) = \dfrac{S(-1)(\omega_1^2 S(-1) - S(1)) - S(0)(\omega_1 S(-1) - S(0))}{\omega_1(\omega_1 S(0) - S(1))}$.

1a and 1b yield the same bounds as the case 1) effective distributions with known $S(-1)$, $S(0)$ and $S(-1)$, $S(0)$, $S(1)$, $S(2)$ respecetively. 2a and 2b 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. Bound 1a was first noticed by Kirkwood[29] and Vinti[30] in 1932. Bound 1b was shown by Weinhold[31] in 1968. Bound 2a is rather trivial and bound 2b is the result presented here.

As an application, bounds on the helium atom polarizability shall be obtained. Pekeris[32] has calculated

$S(2) = 30.334$

$S(1) = 4.084$

$S(0) = 2.000$

$S(-1) = 1.505$

and ω_1 is known[33] to be .7797 a.u. Performing the calculations using the previous equations one finds

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

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

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

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

as compared with the actual value[34] of $S(-2) = 1.383$. The $S'_{1b}(-2)$ and $S'_{2b}(-2)$ yield tighter bounds than $S'_{1a}(-2)$ and $S'_{2a}(-2)$, 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[35]

$$f_{1s-2p} = .2762$$

$$f_{1s-3p} = .0734$$

and from Moore's tables[33] one finds

$$\omega_{1s-2p} = .7797 \text{ a.u.}$$

$$\omega_{1s-3p} = .8484 \text{ a.u.}$$

$$\omega_{1s-4p} = .8725 \text{ a.u.}$$

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 ω_{1s-4p} for ω_1):

$$S'_{m1a}(-2) = .686$$

$$S'_{m1b}(-2) = .716$$

$$S'_{m2a}(-2) = 1.219$$

$$S'_{m2b}(-2) = .967 .$$

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

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

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

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

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

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

F. 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 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.

The general bounding behavior is indicated in Figures 1 and 2. In Figure 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 Figure 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. This behavior has been proved using moment theory by Langhoff and Yates[36] for the case of regularly spaced k_i. For up to four k_i, Barnsley[37] has shown that this behavior holds even if the k_i are arbitrarily (i.e., not regularly) spaced. The
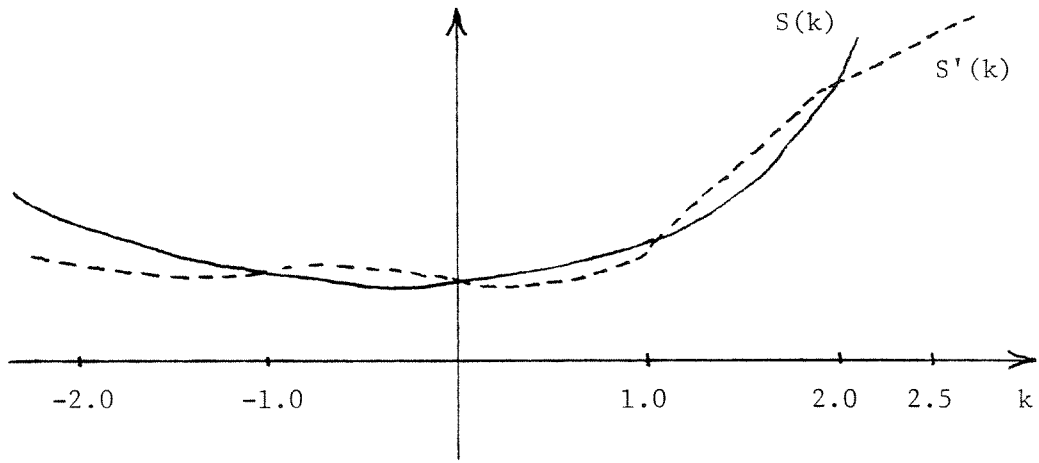
Figure 1

generalization of this behavior for an arbitrarily large number of non-regularly spaced k_i seems likely, although it apparently has not been proven mathematically. In Figure 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
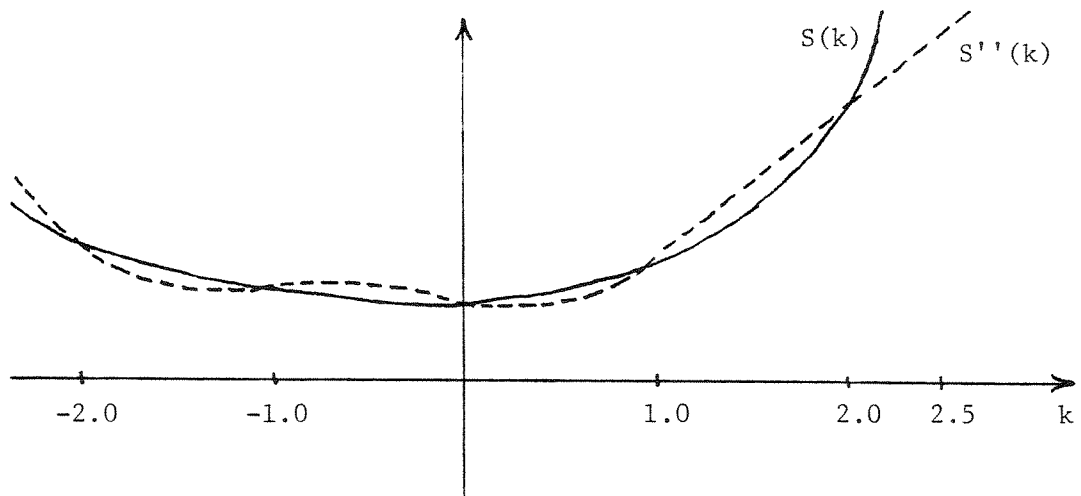
Figure 2

which $S(k_i)$ was used in the construction of the effective distribu-
tion. In this case however, the $S''(k)$ bounds $S(k)$ from above to
the left of the smallest k_i (because case 2) distributions are con-
structed with an odd number of $S(k_i)$). This has also been shown by
Langhoff and Yates[36] for the case of regularly spaced k_i. Again the
generalization for an arbitrarily large number of non-regularly spaced
k_i seems likely, but apparently has not been proven.

As an additional example consider a case 1) distribution con-
structed from $S(1)$, $S(0)$, $S(-1)$ and $S(-2)$. The behavior of the
effective sum $S'''(k)$ constructed from this distribution is illus-
trated in Figure 3. Once both $S''(k)$ (in Figure 2) and $S'''(k)$ (in
Figure 3) are known, both upper and lower bounds have been estab-
lished 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) distributions and
case 2) distributions has already been illustrated by the bounds
derived on the static polarizability in section E.
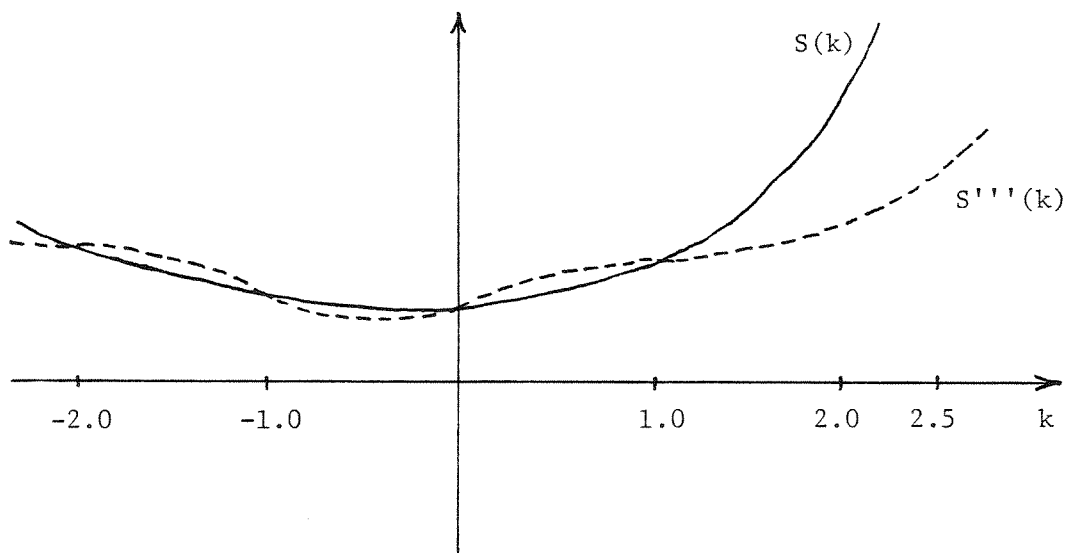
Figure 3

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.

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

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 Figure 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 Figure 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).

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

$$\alpha'(\omega) = \sum_{b=1}^{N} \frac{f'_b}{\omega'^2_b - \omega^2}$$

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 con-
structed from a set which includes certain of the $S(-2)$, $S(-4)$, $S(-6)$,
... then those corresponding terms of the Cauchy expansion for $\alpha'(\omega)$
and $\alpha(\omega)$ will be identical. The reason that case 1) effective dis-
tributions must be used for lower bounds is of course that they gen-
erate 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 reason-
able choice of k_i for the construction of the distribution has been
made. As an example note that the effective distribution of Figure 3
satisfies $S(-2)$ "explicitly" and bounds $S(-4)$, $S(-6)$, ... from below
and therefore generates an effective dynamic polarizability which
bounds the actual dynamic polarizability from below. A similar argu-
ment 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 dyanamic polarizability. The distribution of Figure 2 satis-
fies $S(-2)$ "explicitly" and bounds $S(-4)$, $S(-6)$, ... from above, so
the effective dynamic polarizability corresponding to this distribu-
tion is seen to bound the actual dynamic polarizability from above.
Identical arguments can be made to determine effective Verdet con-
stants 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 $S(-2)$, $S(-4)$, $S(-6)$, ... allows one to arbitrarily closely approach the exact function, not only by equalling the Cauchy series term by term for those $S(-2)$, $S(-4)$, $S(-6)$, ... 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[38], Gordon[23] and Luyckx, et.al.[39] 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:

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

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

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

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

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

etc. and

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

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

Upper bounds on C_6 may be obtained from:

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

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

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

As usual, the $C_6^!$ is constructed by replacing the actual distributions in equation (13) by the effective distribution.

G. 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, ... These $S(k)$ have been shown to be calculable in rational fraction form by Dalgarno and Kingston[40] who list $S(2)$, $S(1)$, ..., $S(-6)$. Gavrila[41] has computed $S(-7)$, ..., $S(-10)$. Gavrila's value of $S(-10)$ contains a typographical error in the numerator which is listed correctly here. In addition $S(-11)$, ..., $S(-15)$ has 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 $S(-11)$, ..., $S(-15)$ calculated here:

$$S(2) \quad = \quad 4/3$$
$$S(1) \quad = \quad 2/3$$
$$S(0) \quad = \quad 1$$
$$S(-1) \quad = \quad 2$$
$$S(-2) \quad = \quad 9/2$$
$$S(-3) \quad = \quad 43/4$$
$$S(-4) \quad = \quad 319/12$$
$$S(-5) \quad = \quad 9673/144$$
$$S(-6) \quad = \quad 297541/1728$$
$$S(-7) \quad = \quad 9243157/20736$$
$$S(-8) \quad = \quad 289165453/248832$$
$$S(-9) \quad = \quad 45,464,213,273/14,929,920$$
$$S(-10) \quad = \quad 7,175,468,425,141/895,795,200$$
$$S(-11) \quad = \quad \frac{1,135,753,416,866,657}{53,747,712,000}$$

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

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

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

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

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

$$S(-16) = 2.767867752796214680257191 \times 10^6$$
$$S(-17) = 7.359191237809297517598849 \times 10^6$$
$$S(-18) = 1.957712849836060068184363 \times 10^7 .$$

For the construction of the case 2) distributions it is also necessary to known that $\omega_1 = 3/8$ 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) distributions 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 1 includes the polynomial equations for case 1) distributions using the set of sums $S(2)$, $S(1)$, ... Table 2 includes the polynomial equations for case 1) distributions satisfying the set of sums $S(1)$, $S(0)$, ... Table 3 includes the polynomial equations for case 2) distributions using the set of sums $S(2)$, $S(1)$, ... Table 4 includes the polynomial equations for case 2) distributions satisfying the set of sums $S(1)$, $S(0)$, ...

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

Table 1

$S(2) - S(1)$: $(2/3)(\omega-2)$

$S(2) - S(-1)$: $(1/9)(3\omega^2-18\omega+8)$

$S(2) - S(-3)$: $(1/(2^2\times9))(3\omega^3-36\omega^2+44\omega-12)$

$S(2) - S(-5)$: $(1/(2^6\times27))(15\omega^4-300\omega^3+700\omega^2-476\omega+96)$

$S(2) - S(-7)$: $(5/(2^{13}\times81))(45\omega^5-1,350\omega^4+5,100\omega^3-6,228\omega^2+2,968\omega-480)$

$S(2) - S(-9)$: $(5/(2^{22}\times81))(315\omega^6-13,230\omega^5+73,500\omega^4-139,356\omega^3$

$\qquad\qquad +114,808\omega^2-42,432\omega+5,760)$

$S(2) - S(-11)$: $(35/(2^{31}\times243))(315\omega^7-17,640\omega^6+135,240\omega^5-365,736\omega^4$

$\qquad\qquad +454,672\omega^3-283,232\omega^2+85,896\omega-10,080)$

$S(2) - S(-13)$: $(35/(2^{42}\times729))(2,835\omega^8-204,120\omega^7+2,063,880\omega^6$

$\qquad\qquad -7,525,224\omega^5+13,051,152\omega^4-12,025,440\omega^3$

$\qquad\qquad +6,037,448\omega^2-1,557,216\omega+161,280)$

$S(2) - S(-15)$: $(35/(2^{57}\times243))(14,175\omega^9-1,275,750\omega^8+16,443,000\omega^7$

$\qquad\qquad -77,633,640\omega^6+178,338,240\omega^5-225,561,600\omega^4$

$\qquad\qquad +165,067,144\omega^3-69,547,248\omega^2+15,637,824\omega-1,451,520)$

$S(2) - S(-17)$: $(175/(2^{74}\times729))(155,925\omega^{10}-17,151,750\omega^9+274,428,000\omega^8$

$\qquad\qquad -1,627,358,040\omega^7+4,770,865,440\omega^6-7,886,102,400\omega^5$

$\qquad\qquad +7,825,636,184\omega^4-4,752,597,808\omega^3+1,727,754,624\omega^2$

$\qquad\qquad -344,851,200\omega+29,030,400)$

Table 2

$S(1) - S(0)$: $(1/3)(3\omega-2)$

$S(1) - S(-2)$: $(1/(2\times3))(3\omega^2-6\omega+2)$

$S(1) - S(-4)$: $(1/(2^4\times9))(15\omega^3-60\omega^2+52\omega-12)$

$S(1) - S(-6)$: $(5/(2^{10}\times27))(45\omega^4-300\omega^3+480\omega^2-268\omega+48)$

$S(1) - S(-8)$: $(5/(2^{18}\times27))(315\omega^5-3,150\omega^4+7,980\omega^3-7,836\omega^2+3,256\omega-480)$

$S(1) - S(-10)$: $(35/(2^{26}\times81))(315\omega^6-4,410\omega^5+16,170\omega^4-24,276\omega^3$

$+17,200\omega^2-5,724\omega+720)$

$S(1) - S(-12)$: $(35/(2^{36}\times243))(2,835\omega^7-52,920\omega^6+264,600\omega^5-559,944\omega^4$

$+592,272\omega^3-329,024\omega^2+91,656\omega-10,080)$

$S(1) - S(-14)$: $(35/(2^{50}\times81))(14,175\omega^8-340,200\omega^7+2,222,640\omega^6$

$-6,282,360\omega^5+9,190,800\omega^4-7,493,328\omega^3$

$+3,431,176\omega^2-823,968\omega+80,640)$

$S(1) - S(-16)$: $(175/(2^{66}\times243))(155,925\omega^9-4,677,750\omega^8+38,669,400\omega^7$

$-140,457,240\omega^6+270,246,240\omega^5-300,494,880\omega^4$

$+199,378,904\omega^3-77,786,928\omega^2+16,444,224\omega-1,451,520)$

$S(1) - S(-18)$: $(1,925/(2^{83}\times729))(467,775\omega^{10}-17,151,750\omega^9+174,947,850\omega^8$

$-793,096,920\omega^7+1,935,893,520\omega^6-2,797,886,520\omega^5$

$+2,504,701,032\omega^4-1,402,063,504\omega^3+477,160,272\omega^2$

$-90,204,480\omega+7,257,600)$

Table 3

$S(2)$: $(4/9)(8\omega-3)$

$S(2) - S(0)$: $(4/(27\times13))(8\omega-3)(7\omega-26)$

$S(2) - S(-2)$: $(1/(2\times9\times107))(8\omega-3)(33\omega^2-306\omega+214)$

$S(2) - S(-4)$: $(1/(2^3\times243\times23))(8\omega-3)(75\omega^3-1,260\omega^2+2,180\omega-828)$

$S(2) - S(-6)$: $(25/(2^{12}\times243\times113))(8\omega-3)(285\omega^4-7,500\omega^3+23,200\omega^2$

$\qquad\qquad -20,684\omega+5,424)$

$S(2) - S(-8)$: $(5/(2^{20}\times81\times503))(8\omega-3)(7,245\omega^5-274,050\omega^4+1,312,500\omega^3$

$\qquad\qquad -2,015,748\omega^2+1,200,008\omega-241,440)$

$S(2) - S(-10)$: $(245/(2^{30}\times243\times233))(8\omega-3)(945\omega^6-48,510\omega^5+330,750\omega^4$

$\qquad\qquad -764,988\omega^3+764,592\omega^2-341,524\omega+55,920)$

$S(2) - S(-12)$: $(35/(2^{38}\times3^7\times103))(8\omega-3)(9,765\omega^7-652,680\omega^6+5,991,720\omega^5$

$\qquad\qquad -19,311,096\omega^4+28,481,008\omega^3-20,976,320\omega^2+7,505,208\omega$

$\qquad\qquad -1,038,240)$

$S(2) - S(-14)$: $(35/(2^{5\ 6}\times3^4\times1,187))(8\omega-3)(496,125\omega^8-41,844,600\omega^7$

$\qquad\qquad +496,918,800\omega^6-2,119,922,280\omega^5+4,285,416,240\omega^4$

$\qquad\qquad -4,588,475,760\omega^3+2,671,342,616\omega^2-798,061,536\omega$

$\qquad\qquad +95,719,680)$

$S(2) - S(-16)$: $(875/(2^{72}\times3^7\times17\times29)(8\omega-3)(2,027,025\omega^9-210,498,750\omega^8$

$\qquad\qquad +3,137,211,000\omega^7-17,074,161,720\omega^6+45,066,589,920\omega^5$

$\qquad\qquad -65,317,111,200\omega^4+54,664,675,832\omega^3-26,306,177,904\omega^2$

$\qquad\qquad +6,752,250,432\omega-715,599,360)$

Table 4

S(1): $(2/9)(8\omega-3)$

S(1) - S(-1): $(1/(9\times7))(8\omega-3)(6\omega-7)$

S(1) - S(-3): $(1/(2^3\times9\times11))(8\omega-3)(15\omega^2-45\omega+22)$

S(1) - S(-5): $(1/(2^8\times81))(8\omega-3)(30\omega^3-165\omega^2+194\omega-60)$

S(1) - S(-7): $(25/(2^{17}\times81\times19))(8\omega-3)(315\omega^4-2,730\omega^3+5,628\omega^2$

$-4,012\omega+912)$

S(1) - S(-9): $(35/(2^{25}\times81\times23))(8\omega-3)(630\omega^5-7,875\omega^4+24,780\omega^3$

$-30,012\omega^2+15,302\omega-2,760)$

S(1) - S(-11): $(245/(2^{35}\times3^9))(8\omega-3)(2,835\omega^6-48,195\omega^5+213,570\omega^4$

$-385,344\omega^3+326,682\omega^2-129,708\omega+19,440)$

S(1) - S(-13): $(35/(2^{47}\times3^5\times31))(8\omega-3)(28,350\omega^7-628,425\omega^6+3,717,630\omega^5$

$-9,266,040\omega^4+11,500,110\omega^3$

$-7,475,876\omega^2+2,433,096\omega-312,480)$

S(1) - S(-15): $(5/(2^{65}\times81))(8\omega-3)(155,925\omega^8-4,365,900\omega^7+33,180,840\omega^6$

$-108,690,120\omega^5+183,676,680\omega^4-172,555,968\omega^3$

$+90,894,008\omega^2-25,089,120\omega+2,822,400)$

S(1) - S(-17): $(9,625/(2^{82}\times3^7\times13))(8\omega-3)(311,850\omega^9-10,758,825\omega^8$

$+102,037,320\omega^7-423,866,520\omega^6+930,055,500\omega^5$

$-1,176,714,864\omega^4+886,939,840\omega^3-392,713,992\omega^2$

$+94,186,656\omega-9,434,880)$

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.[39] can be used to obtain both upper and lower bounds on the C_6 coefficient. Table 5 lists the values of C_6 obtained from the effective distributions. All values obtained from the $S(2) - S(3-2N)$ distributions, with the exception of the $S(2) - S(1)$ 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[42] has calculated C_6 to 11 digits as 6.4990267054. 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 Table 6 and Table 7. The actual values have been taken from Shimamura[43]. 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[44] yields an effective oscillator strength distribution which satisfies $S(0)$, $S(-1)$, $S(-2)$, $S(-3)$, ... (this will be discussed in Chapter III). 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.

Table 5

Sums Included	C_6
S(2) — S(1)	.0104166667
S(2) — S(-1)	6.1718750000
S(2) — S(-3)	6.4869186047
S(2) — S(-5)	6.4985858385
S(2) — S(-7)	6.4990079440
S(2) — S(-9)	6.4990256449
S(2) — S(-11)	6.4990266196
S(2) — S(-13)	6.4990266957
S(2) — S(-15)	6.4990267040
S(2) — S(-17)	6.4990267051
S(1) — S(0)	2.5312500000
S(1) — S(-2)	6.5625000000
S(1) — S(-4)	6.5012755102
S(1) — S(-6)	6.4991142052
S(1) — S(-8)	6.4990309493
S(1) — S(-10)	6.4990269921
S(1) — S(-12)	6.4990267331
S(1) — S(-14)	6.4990267091
S(1) — S(-16)	6.4990267060
S(1) — S(-18)	6.4990267055

Table 6

Sums Included	L(-1)	L(0)	L(1)	L(2)
S(2) - S(1)	.1155245	.46210	1.848	7.39
S(2) - S(0)	-.3264946	-.08740	1.104	9.52
S(2) - S(-1)	-.0257520	.05486	.933	10.61
S(2) - S(-2)	-.0681191	.08574	.846	11.59
S(2) - S(-3)	-.0715828	.09134	.820	12.03
S(2) - S(-4)	-.0728482	.09478	.796	12.60
S(2) - S(-5)	-.0730491	.09557	.788	12.85
S(2) - S(-6)	-.0731848	.09631	.779	13.23
S(2) - S(-7)	-.0732116	.09650	.776	13.38
S(2) - S(-8)	-.0732365	.09672	.771	13.65
S(2) - S(-9)	-.0732420	.09678	.770	13.75
S(2) - S(-10)	-.0732482	.09686	.768	13.95
S(2) - S(-11)	-.0732497	.09689	.767	14.03
S(2) - S(-12)	-.0732517	.09692	.766	14.18
S(2) - S(-13)	-.0732522	.09693	.765	14.24
S(2) - S(-14)	-.0732529	.09695	.764	14.37
S(2) - S(-15)	-.0732531	.09695	.764	14.41
S(2) - S(-16)	-.0732533	.09696	.763	14.51
S(2) - S(-17)	-.0732534	.09696	.763	14.55
Actual	-.0732538	.09698	.761	15.92

Table 7

Sums Included	L(-1)	L(0)	L(1)	L(2)
S(1) - S(0)	.2157671	.28768	.384	.51
S(1) - S(-1)	-.1084747	.13047	.592	1.60
S(1) - S(-2)	-.0798449	.11024	.654	2.32
S(1) - S(-3)	-.0744666	.10150	.701	3.35
S(1) - S(-4)	-.0737740	.09962	.716	3.87
S(1) - S(-5)	-.0734070	.09815	.732	4.73
S(1) - S(-6)	-.0733404	.09778	.738	5.12
S(1) - S(-7)	-.0732864	.09739	.745	5.82
S(1) - S(-8)	-.0732750	.09729	.747	6.12
S(1) - S(-9)	-.0732631	.09716	.751	6.71
S(1) - S(-10)	-.0732604	.09712	.752	6.95
S(1) - S(-11)	-.0732570	.09707	.755	7.44
S(1) - S(-12)	-.0732562	.09705	.755	7.64
S(1) - S(-13)	-.0732551	.09703	.757	8.06
S(1) - S(-14)	-.0732548	.09702	.757	8.22
S(1) - S(-15)	-.0732544	.09701	.758	8.58
S(1) - S(-16)	-.0732542	.09700	.758	8.72
S(1) - S(-17)	-.0732540	.09700	.759	9.03
S(1) - S(-18)	-.0732540	.09700	.759	9.15
Actual	-.0732538	.09698	.761	15.92

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CHAPTER III
VARIATIONAL CALCULATIONS OF MULTIPOLE OSCILLATOR STRENGTH SUMS, LOGARITHMIC MEAN EXCITATION ENERGIES, AND OTHER SECOND ORDER PERTURBATION QUANTITIES

A. INTRODUCTION

In Chapter II a method has been given for constructing an effective spectrum from a set of dipole oscillator strength sums, which allows the determination of bounds on certain properties of atoms and molecules arising from second order perturbation theory. Given an ab initio wavefunction for the ground state, only four oscillator strength sums, $S(2)$, $S(1)$, $S(0)$ and $S(-1)$, may be written as expectation values of the wavefunction. To obtain additional sums one must either rely upon experiment or calculate the sums variationally. A procedure for performing variational calculations of the dipole oscillator strength sums is presented in the present chapter.

Matrix elements of higher order multipole operators are required for the calculation of corrections beyond the dipole approximation in both static electric field problems (such as multipole polarizabilities, Van der Waals coefficients, etc.) and problems involving the interaction of radiation with atoms and molecules. In static electric field problems involving S-state atoms, selection rules can be used to show that all second order perturbation quantities are expressible in terms of the modulus squared of matrix elements of electric multipole operators. For these cases the multipole generalization of the dipole oscillator strength, i.e. the multipole oscillator strength, proves to be a convenient quantity with which to evaluate perturbation expressions. A definition of multipole oscillator strengths is developed, along with application to the computation of multipole polarizabilities and the C_6, C_8 and C_{10} coefficients required for the long range expansion of the Van der Waals

B.   VARIATIONAL CALCULATIONS OF DIPOLE OSCILLATOR STRENGTH SUMS

In the length form of the dipole matrix element, $S(k)$ may be written as

$$S(k) = \sum_i f_{oi} \, \omega_{oi}^k \tag{1}$$

$$= \sum_i \frac{2}{3} |\langle \Psi_o | \sum_{\mu=1}^{N} \vec{r}_{(\mu)} | \Psi_i \rangle|^2 (E_i - E_o)^{k+1} . \tag{2}$$

Following Dalgarno[5], note that for negative arguments only, $S(-k-1)$ (for $k = 0, 1, 2, \ldots$) may be written

$$S(-k-1) = \langle \chi_k | \chi_o \rangle = \langle \chi_{k-1} | \chi_1 \rangle = \cdots = \langle \chi_o | \chi_k \rangle \tag{3}$$

where

$$|\chi_o\rangle = \left(\frac{2}{3}\right)^{\frac{1}{2}} \sum_{\mu=1}^{N} \vec{r}_{(\mu)} |\Psi_o\rangle \tag{4}$$

and $|\chi_n\rangle$ is defined to be the solution of

$$(H - E_o)|\chi_n\rangle - |\chi_{n-1}\rangle = 0 \tag{5}$$

where H is the Hamiltonian and E_0 is the energy of state $|\Psi_o\rangle$. Note that the $|\chi_i\rangle$ are three component kets. The Dirac bracket is computed by taking the dot product between the ket vector and the bra vector, i.e. by taking the sum of the three Dirac brackets formed from corresponding components of the bra and ket vectors. The operator $(H - E_0)$ is positive on the space of functions orthogonal to the ground state wavefunction, therefore if a solution exists in this space, it is unique[6].

It proves useful to consider the functional

$$V_n(\xi) = \langle \xi | (E_o - H)|\xi\rangle + 2\langle \xi | \chi_{n-1} \rangle . \tag{6}$$

If equation (5) has a solution, then this functional is stationary

(i.e. the first variation δv_n of v_n vanishes) for $|\xi\rangle = |\chi_n\rangle$. Conversely, a function for which this functional is stationary satisfies equation (5). These claims are proved as follows. To obtain the variations of the functional[7], $v_n(\chi_n + \epsilon\Omega)$ must be expanded in a Taylor series in ϵ :

$$V_n(\chi_n + \epsilon\Omega) = V_n(\chi_n) + \epsilon V_{n1}(\chi_n, \Omega) + \tfrac{1}{2}\epsilon^2 V_{n2}(\chi_n, \Omega) + \cdots . \tag{7}$$

Note that the expansion defines the functionals v_{n1} and v_{n2}. The first variation δv_n of v_n is defined by $\delta v_n = \epsilon v_{n1}(\chi_n, \Omega)$. The second variation $\delta^2 v_n$ of v_n is defined by $\delta^2 v_n = (1/2)\epsilon^2 v_{n2}(\chi_n, \Omega)$. Performing the expansion in order to make the identifications leads to

$$V_n(\chi_n + \epsilon\Omega) = (\langle\chi_n| + \epsilon\langle\Omega|)(E_o - H)(|\chi_n\rangle + \epsilon|\Omega\rangle) + 2(\langle\chi_n| + \epsilon\langle\Omega|)|\chi_{n-1}\rangle \tag{8}$$

$$= \langle\chi_n|(E_o - H)|\chi_n\rangle + 2\langle\chi_n|\chi_{n-1}\rangle$$
$$+ \epsilon\left(2\langle\Omega|(E_o - H)|\chi_n\rangle + 2\langle\Omega|\chi_{n-1}\rangle\right)$$
$$+ \tfrac{1}{2}\epsilon^2\left(2\langle\Omega|(E_o - H)|\Omega\rangle\right) . \tag{9}$$

Therefore

$$\delta V_n = 2\epsilon\langle\Omega|\left((E_o - H)|\chi_n\rangle + |\chi_{n-1}\rangle\right) \tag{10}$$

and

$$\delta^2 V_n = \epsilon^2\langle\Omega|(E_o - H)|\Omega\rangle \tag{11}$$

and all higher variations vanish. Inserting equation (5) into equation (10) yields

$$\delta V_n = 2\epsilon\langle\Omega|\left((E_o - H)|\chi_n\rangle + |\chi_{n-1}\rangle\right) = 0 \tag{12}$$

therefore the functional is stationary for $|\xi\rangle = |\chi_n\rangle$. The converse is similarly shown by performing the expansion about an undetermined function for which the functional is required to be stationary. The fact that $\epsilon|\Omega\rangle$ is arbitrary requires that for the first variation to

vanish, the undetermined function must be a solution to equation (5). Note that the exact value of $v_n(\chi_n)$ is just $\langle \chi_n | \chi_{n-1} \rangle = S(-2n)$. Furthermore, once $|\chi_n\rangle$ is obtained, $S(-2n-1)$ may also be calculated from the relation $S(-2n-1) = \langle \chi_n | \chi_n \rangle$.

If $|\chi_{n-1}\rangle$ is exact then a variational calculation of $|\chi_n\rangle$ will lead to a value of v_n such that $v_n \leq S(-2n)$. This follows from equation (11) which indicates that the second variation is always negative. Therefore any deviation from the stationary position of v_n (where $v_n = S(-2n)$) will tend to decrease v_n, so the stationary position is indeed a maximum. Since all variations beyond the second vanish, the maximum is not only local but in fact global. Therefore if a finite set of trial functions is capable of representing $|\chi_n\rangle$ exactly then $v_n = S(-2n)$ and if it is not then $v_n < S(-2n)$ (in which case the v_n obtained is the maximum possible value with respect to the subspace of trial functions). Apparently no such bound exists for $S(-2n-1)$ calculated in terms of a variational approximation to $|\chi_n\rangle$.

In order to explicitly perform a variational calculation, a choice for the functional form of the trial functions must first be made. Here a linear form for the trial functions is assumed, i.e. $|\chi_n\rangle$ is approximated by $|\chi_n'\rangle$ where

$$|\chi_n'\rangle = \sum_{i=1}^{r} a_i^{(n)} | \phi_i \rangle \tag{13}$$

and $\{|\phi_i\rangle\}$ $i = 1, 2, \ldots, r$, are a set of basis functions of the correct symmetry. Then the $a_i^{(n)}$'s for which v_n is stationary are determined by solving the system

$$\frac{\partial v_n}{\partial a_i^{(n)}} = 0 \qquad i = 1, 2, \cdots, r. \tag{14}$$

Note that if the $\{|\phi_i\rangle\}$ satisfy $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ and $\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i$ (which can be accomplished by a Gramm-Schmidt orthogonalization followed by a unitary transformation on a basis set

which doesn't satisfy these requirements) then

$$O = \frac{\partial v_n}{\partial a_i^{(n)}}$$

$$= -2 \langle \phi_i | (\epsilon_i - E_o) | \phi_i \rangle a_i^{(n)} + 2 \langle \phi_i | \chi_{n-1} \rangle \tag{15}$$

so,

$$a_i^{(n)} = (\epsilon_i - E_o)^{-1} \langle \phi_i | \chi_{n-1} \rangle. \tag{16}$$

However in practice, only a variational approximation $|\chi'_{n-1}\rangle$ to the $|\chi_{n-1}\rangle$ appearing in equations (15) and (16) will be known, hence a more appropriate functional to consider is $v'_n(\xi)$, where

$$v'_n(\xi) = \langle \xi | (E_o - H) | \xi \rangle + 2 \langle \xi | \chi'_{n-1} \rangle. \tag{17}$$

Similarly, the $a_i^{(n)}$'s for which v'_n is stationary are given by

$$a_i^{(n)} = (\epsilon_i - E_o)^{-1} \langle \phi_i | \chi'_{n-1} \rangle. \tag{18}$$

Therefore,

$$|\chi'_n\rangle = \sum_{i=1}^{r} (\epsilon_i - E_o)^{-1} \langle \phi_i | \chi'_{n-1} \rangle | \phi_i \rangle \tag{19}$$

and by recurring upward from $|\chi'_o\rangle = |\chi_o\rangle$ it is straightforward to find that in terms of $|\chi_o\rangle$,

$$|\chi'_n\rangle = \sum_{i=1}^{r} (\epsilon_i - E_o)^{-n} \langle \phi_i | \chi_o \rangle | \phi_i \rangle. \tag{20}$$

Utilizing this result to evaluate equation (3) it is found that the k + 1 possible forms for calculating the approximation S'(-k-1) to S(-k-1) using $|\chi_o\rangle$ and the functions $|\chi'_1\rangle, |\chi'_2\rangle, \ldots, |\chi'_k\rangle$ all yield the same result,

$$S'(-k-1) = \sum_{i=1}^{r} (\epsilon_i - E_o)^{-k} |\langle \phi_i | \chi_o \rangle|^2 \tag{21}$$

$$= \frac{2}{3} \sum_{i=1}^{r} (\epsilon_i - E_o)^{-k} \left| \langle \phi_i | \sum_{\mu=1}^{N} \vec{r}_{(\mu)} | \psi_o \rangle \right|^2 \qquad (22)$$

for $\{ | \phi_j \rangle \}$ such that $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ and $\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i$.
Finally, note that Dalgarno and Epstein[8] have proven:

1. If the basis spans

$$\sum_{\mu=1}^{N} \vec{r}_{(\mu)} | \psi_o \rangle$$

then $S(-1)$ and $S(0)$ must be satisfied.

2. If the basis spans

$$\sum_{\mu=1}^{N} \vec{r}_{(\mu)} | \psi_o \rangle$$

and

$$\sum_{\mu=1}^{N} \vec{\nabla}_{(\mu)} | \psi_o \rangle$$

then $S(-1)$, $S(0)$, $S(1)$ and $S(2)$ must be satisfied.

C. MULTIPOLE OSCILLATOR STRENGTHS AND OSCILLATOR STRENGTH SUMS

Let $Q^{(j)}$ be a 2^j-pole operator of the form

$$Q^{(j)} = \sum_{\mu=1}^{N} \sum_{\tau=-j}^{j} a_\tau \, r_{(\mu)}^{j} \, Y_{j\tau(\mu)} \qquad (23)$$

where $r_{(\mu)}$ is the radial coordinate associated with the μth electron
and $Y_{j\tau(\mu)}$ is the spherical harmonic associated with the μth elec-
tron. Then the oscillator strength of $Q^{(j)}$ associated with the tran-
sition from $|n\ell m\rangle$ to $|n'\ell'm'\rangle$ is given by

$$f_{n\ell m, n'\ell'm'}(Q^{(j)}) = 2 \left| \langle n'\ell'm' | Q^{(j)} | n\ell m \rangle \right|^2 \omega_{n\ell m, n'\ell'm'} . \qquad (24)$$

It is desirable to expand $f_{nlm,n'l'm'}(Q^{(j)})$ in terms of the matrix

elements of the basis

$$\sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j\tau(\mu)} \quad , \quad \tau = j, \cdots, -j$$

so equation (24) may be rewritten as

$$f_{n\ell m, n'\ell'm'} \left(Q^{(j)} \right)$$

$$= 2 \langle n\ell m | \sum_{\nu=1}^{N} \sum_{\sigma=-j}^{j} a_{\sigma}^{*} r_{(\nu)}^{j} Y_{j\sigma(\nu)}^{*} | n'\ell'm' \rangle \times$$

$$\times \langle n'\ell'm' | \sum_{\mu=1}^{N} \sum_{\tau=-j}^{j} a_{\tau} r_{(\mu)}^{j} Y_{j\tau(\mu)} | n\ell m \rangle \; \omega_{n\ell m, n'\ell'm'} \quad (25)$$

$$= 2 \sum_{\sigma=-j}^{j} \sum_{\tau=-j}^{j} a_{\sigma}^{*} a_{\tau} \langle n\ell m | \sum_{\nu=1}^{N} r_{(\nu)}^{j} Y_{j\sigma(\nu)}^{*} | n'\ell'm' \rangle \times$$

$$\times \langle n'\ell'm' | \sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j\tau(\mu)} | n\ell m \rangle \; \omega_{n\ell m, n'\ell'm'}. \quad (26)$$

The Wigner-Eckart Theorem allows one to write

$$\langle n'\ell'm' | T_{k}^{(J)} | n\ell m \rangle = \langle \ell m J k | \ell'm' \rangle \langle n'\ell' | T^{(J)} | n\ell \rangle \quad (27)$$

where $\langle \ell m J k | \ell'm' \rangle$ is a Clebsch-Gordan coefficient and $\langle n'\ell' | T^{(J)} | n\ell \rangle$ is the reduced matrix element. However the Clebsch-Gordan coefficient is non-zero only if $m + k = m'$. Hence the summation in equation (26) may be rewritten as

$$f_{n\ell m, n'\ell'm'} \left(Q^{(j)} \right)$$

$$= 2 | a_{m'-m} |^{2} \langle n\ell m | \sum_{\nu=1}^{N} r_{(\nu)}^{j} Y_{j \, m'-m \, (\mu)}^{*} | n'\ell'm' \rangle \times$$

$$\times \langle n'\ell'm' | \sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j \, m'-m \, (\mu)} | n\ell m \rangle \; \omega_{n\ell m, n'\ell'm'} \quad (28)$$

$$= 2 | a_{m'-m} |^{2} | \langle n'\ell'm' | \sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j \, m'-m \, (\mu)} | n\ell m \rangle |^{2} \omega_{n\ell m, n'\ell'm'} \quad (29)$$

where $Y_{j \, m'-m \, (\mu)} = 0$ if $|m' - m| > j$ here by definition. Therefore the oscillator strength for any 2^{j}-pole operator of the form (23) may be evaluated if the oscillator strengths of the basis elements

$$\sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j\tau(\mu)},$$

$$f_{n\ell m,n'\ell'm'} \left(\sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j\tau(\mu)} \right)$$

$$= 2 \left| \langle n'\ell'm' | \sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j\tau(\mu)} | n\ell m \rangle \right|^{2} \omega_{n\ell m,n'\ell'm'} \qquad (30)$$

are known for all $-j \leqslant \tau \leqslant j$.

The dipole oscillator strength is frequently written in the form

$$f_{n\ell m,n'\ell'm'}$$

$$= \frac{2}{3} \left\{ \left| \langle n'\ell'm' | \sum_{\mu=1}^{N} x_{\mu} | n\ell m \rangle \right|^{2} + \left| \langle n'\ell'm' | \sum_{\mu=1}^{N} y_{\mu} | n\ell m \rangle \right|^{2} \right.$$

$$\left. + \left| \langle n'\ell'm' | \sum_{\mu=1}^{N} z_{\mu} | n\ell m \rangle \right|^{2} \right\} \omega_{n\ell m,n'\ell'm'} \qquad (31)$$

which can be rewritten in terms of spherical tensors as

$$f_{n\ell m,n'\ell'm'}$$

$$= \frac{8\pi}{9} \sum_{\tau=-1}^{1} \left| \langle n'\ell'm' | \sum_{\mu=1}^{N} r_{(\mu)} Y_{1\tau(\mu)} | n\ell m \rangle \right|^{2} \omega_{n\ell m,n'\ell'm'}. \qquad (32)$$

Apparently a consistent generalization of this definition of the dipole oscillator strength to 2^{j}-pole operators which maintains the rotational invariance of the matrix elements is given by

$$f_{n\ell m,n'\ell'm'}^{(j)}$$

$$= \frac{8\pi}{(2j+1)^{2}} \sum_{\tau=-j}^{j} \left| \langle n'\ell'm' | \sum_{\mu=1}^{N} r_{(\mu)}^{j} Y_{j\tau(\mu)} | n\ell m \rangle \right|^{2} \omega_{n\ell m,n'\ell'm'}. \qquad (33)$$

The utility of this expression, however, can only be determined by examining the specific problem requiring the evluation of the oscillator strengths. The definition in equation (24) contains more in-

formation but the definition in equation (33) may be sufficient. Another modification of the original definition (24) of the oscillator strength is to average over the orientations of $|n\ell m\rangle$ and $|n'\ell'm'\rangle$. For details see references (9) and (10).

At this point the situations in which the concept of multipole oscillator strengths is useful for the evaluation of second order perturbation expressions shall be examined. Assume a perturbation V is given to be added to an unperturbed Hamiltonian H_0. In order to implement second order perturbation theory one must evaluate expressions of the form

$$|V_{n\ell m, n'\ell'm'}|^2 = |\langle n'\ell'm'|V|n\ell m\rangle|^2. \tag{34}$$

In many cases the perturbation V can be written in the form of a multipole expansion

$$V = \sum_{i=1}^{\infty} a_i \, Q^{(i)} \tag{35}$$

where the a_i are "constants" (i.e. they do not include any of the variables integrated over for the calculation of the matrix element) which parameterize the strength of the perturbation. Therefore equation (34) may be rewritten as

$$|V_{n\ell m, n'\ell'm'}|^2$$

$$= \sum_{k=1}^{\infty} \sum_{i=1}^{\infty} a_k^* \, a_i \, \langle n\ell m| Q^{(k)*} |n'\ell'm'\rangle \times$$

$$\times \langle n'\ell'm'|Q^{(i)}|n\ell m\rangle. \tag{36}$$

For the multipole expansion to be useful the a_i's must decrease in magnitude rapidly enough with increasing i such that a small number of terms is sufficient to furnish an accurate approximation to the actual V. This decrease in magnitude of the a_i's usually comes about through the appearance of a parameter of "smallness" ϵ (< 1)

raised to a power. The power is a strictly increasing function of the index i of a_i. The truncation of the series (35) may be performed consistently by choosing a value p for the maximum power of ϵ desired, then including all terms $a_k^* a_i$ containing ϵ to a power less than or equal to p. Corrections from third and higher orders of perturbation theory which contribute terms containing ϵ to a power less than or equal to p must also be included for a consistent expansion. This complication of contributions from higher orders of perturbation theory, however, shall be ignored in the following discussion.

The oscillator strengths as defined previously are proportional to the modulus squared of the matrix element of an operator. Evaluation of the above expression apparently requires terms which are not of the modulus squared form (i.e. are proportional to the product of matrix elements associated with two different operators). These "cross terms" can be calculated in addition to the oscillator strengths if required and in fact sum rules can also be derived for these terms[5]. However for simplicity this discussion shall be limited to cases where only terms of the multipole oscillator strength form appear in the summation. In the following shall be described two situations where cross terms are not required in the evaluation of the above expansion.

First, the most obvious case for which the cross terms need not be considered is when only the dominant operator (i.e. the first operator in the multipole expansion which is allowed by the selection rules) associated with the transition is included in the expansion. Since other nonvanishing operators will be multiplied by coefficients containing the smallness parameter to higher powers, truncating the series at the first term is consistent.

If higher order contributions to the expansion are desired, rotational symmetry can be utilized to show that the cross terms vanish in the event that one of the states involved in the transition is an S-state. This claim shall be proven below using the

Wigner-Eckart Theorem. Note that if neither of the states involved in the transition is an S-state then in general the cross terms will not vanish. Fortunately the ground states of more than half of the first twenty neutral atoms and their positive ions have S symmetry[11] so this discussion is of practical interest.

From the Wigner-Eckart Theorem one again has equation (27),

$$\langle n'\ell'm' | T_k^{(J)} | n\ell m \rangle = \langle \ell m \, Jk \, | \, \ell'm' \rangle \langle n'\ell' | T^{(J)} | n\ell \rangle.$$

The nonvanishing Clebsch-Gordan coefficients satisfy the triangle condition $|1 - 1'| < J < 1 + 1'$. In the event that $|n\ell m\rangle$ is an S-state then $1 = 0$ which implies $J = 1'$. In this case the product of matrix elements $\langle n00 | Q^{(k)*} | n'\ell'm' \rangle \langle n'\ell'm' | Q^{(i)} | n00 \rangle$ is nonvanishing only for $i = k = 1'$ hence cross terms cannot appear in the expansion (36). If one of the states is not an S-state then in general cross terms will occur. The Wigner-Eckart Theorem is nevertheless useful for reducing the number of terms which must be considered. Also, since the eigenstates must be of a definite parity, Laporte's rule can be used to eliminate still more terms. For example, Laporte's rule implies that cross terms involving a dipole and a quadrupole operator must vanish (for the dipole and quadrupole operators of the form defined in equation (23)).

Having defined the multipole oscillator strength in equation (30) the multipole analogue of the dipole oscillator strength sum is simple to construct. The multipole oscillator strength sum of the operator $Q^{(j)}$ may be defined as

$$S_{n\ell m}(k; Q^{(j)}) = \sum_{n'\ell'm'} f_{n\ell m, n'\ell'm'}(Q^{(j)}) \, \omega_{n\ell m, n'\ell'm'}^k. \tag{37}$$

Sum rules for multipole oscillator strength sums are constructed in the same way as for the dipole sums. In section H the sum rules for quadrupole oscillator strength sums shall be computed explicitly. Finally, it should be noted that the variational approach described in section B for the calculation of dipole sums can be trivially al-

tered for the calculation of multipole sums. All that must be done is to replace the operator

$$\left(\frac{2}{3}\right)^{\frac{1}{2}} \sum_{\mu=1}^{N} \vec{r}_{(\mu)}$$

by

$$2^{\frac{1}{2}} Q^{(j)}.$$

D. VARIATIONAL CALCULATIONS OF MULTIPOLE OSCILLATOR STRENGTH SUMS FOR ATOMIC HYDROGEN

It has long been known[12-13] that if the operational procedure described in section B is applied to the ground state of atomic hydrogen then a properly chosen variational basis satisfies certain dipole $S(k)$ exactly. The "proof" of this rule has apparently only been "derived" from empirical observations of numerical calculations. In this section shall be presented a simple mathematical explanation of why the exact satisfaction of certain dipole sums must indeed follow for the hydrogen ground state if the basis is constructed properly. The argument is easily extended to deal with variational calculations of multipole sums for the ground state of hydrogen. For simplicity, the derivation will first be performed for only the case of the dipole operator $r \cos\theta$ and the extension to the arbitrary multipole case will follow by analogy.

The values of the dipole oscillator strength sum

$$S(-t) = \sum_{m} 2|\langle \Psi_{m}|r\cos\theta|\Psi_{o}\rangle|^{2}(E_{m}-E_{o})^{1-t} \tag{38}$$

are desired for $t = 1, 2, 3, \ldots$. The ket $|\Psi_{o}\rangle$ denotes the ground state of hydrogen. Dalgarno and Kingston[14] show that this problem can be converted into one of solving an inhomogeneous differential equation. Define $u_{k}(\vec{r})$ to be the solution of the equation

$$\Psi_0 \nabla^2 u_k + 2(\vec{\nabla}\Psi_0)\cdot(\vec{\nabla}u_k) = -\Psi_0 u_{k-1} \tag{39}$$

and

$$u_0 = 2^{\frac{1}{2}} r\cos\theta. \tag{40}$$

The solution may be shown to be of the form

$$u_k(\vec{r}) = \left(a_{k+1}^{(k)} r^{k+1} + a_k^{(k)} r^k + \cdots + a_1^{(k)} r\right)\cos\theta \tag{41}$$

where the $a_i^{(j)}$'s may be determined recursively. The solution of equation (39) is a function which satisfies the equation

$$\langle \Psi_m | u_k | \Psi_0 \rangle = (E_m - E_0)^{-1} \langle \Psi_m | u_{k-1} | \Psi_0 \rangle \tag{42}$$

for all eigenstates $|\Psi_m\rangle$ (proved by Dalgarno and Lewis[15]). Equations (40) and (42) allow equation (38) to be writen as

$$S(-t) = \langle \Psi_0 | u_0 u_{t-1} | \Psi_0 \rangle = \langle \Psi_0 | u_1 u_{t-2} | \Psi_0 \rangle = \cdots = \langle \Psi_0 | u_{\frac{t-1}{2}}^2 | \Psi_0 \rangle \tag{43}$$

for t odd and

$$S(-t) = \langle \Psi_0 | u_0 u_{t-1} | \Psi_0 \rangle = \langle \Psi_0 | u_1 u_{t-2} | \Psi_0 \rangle = \cdots = \langle \Psi_0 | u_{\frac{t}{2}-1} u_{\frac{t}{2}} | \Psi_0 \rangle \tag{44}$$

for t even.

As described in Section B the oscillator strength sums may also be calculated variationally. The results presented above concerning the exact solution of the S(-t) may be used to determine a variational basis which is also capable of obtaining the S(-t) exactly. As before, the variational basis is required to satisfy

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \tag{45}$$

and

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i . \tag{46}$$

Then the variational solution $S'(-t)$ to the dipole oscillator strength sum $S(-t)$ is given by

$$S'(-t) = \sum_m |\langle \phi_m | r \cos\theta | \Psi_0 \rangle|^2 (\epsilon_m - E_0)^{1-t}. \tag{47}$$

Now note that equation (42) implies that

$$\langle \Psi_m | u_{k-1} | \Psi_0 \rangle = \langle \Psi_m | [H, u_k] | \Psi_0 \rangle. \tag{48}$$

Since this relation holds for all eigenstates $|\Psi_m\rangle$ it must hold for any arbitrary function $|\phi_n\rangle$ which can be written as a linear combination of the $|\Psi_m\rangle$, i.e.

$$\langle \phi_n | u_{k-1} | \Psi_0 \rangle = \langle \phi_n | [H, u_k] | \Psi_0 \rangle \tag{49}$$

for the states $|\phi_n\rangle$ of the variational basis. It is useful to introduce the projection operator associated with the space spanned by the variational basis,

$$P = \sum_n |\phi_n\rangle\langle\phi_n|$$

and also define $H_{PP} = PHP$. Then

$$(\epsilon_n - E_0)\langle \phi_n | u_k | \Psi_0 \rangle = \langle \phi_n | H_{PP} u_k - u_k H | \Psi_0 \rangle \tag{50}$$

follows from equations (45), (46) and the fact that $H|\Psi_0\rangle = E_0|\Psi_0\rangle$. Note that if the set $\{|\phi_n\rangle\}$ contains $u_k|\Psi_0\rangle$ then $Pu_k|\Psi_0\rangle = u_k|\Psi_0\rangle$, and therefore

$$\langle \phi_n | H_{PP} u_k | \Psi_0 \rangle = \langle \phi_n | H u_k | \Psi_0 \rangle. \tag{51}$$

Substituting equation (51) into equation (50), one finds

$$
\begin{aligned}
(\epsilon_n - E_0)\langle \phi_n | u_k | \Psi_0 \rangle &= \langle \phi_n | H u_k - u_k H | \Psi_0 \rangle \\
&= \langle \phi_n | [H, u_k] | \Psi_0 \rangle \\
&= \langle \phi_n | u_{k-1} | \Psi_0 \rangle
\end{aligned}
\tag{52}
$$

where the last step was performed using equation (49).

Hence

$$\langle \phi_n | u_k | \Psi_o \rangle = (\epsilon_n - E_o)^{-1} \langle \phi_n | u_{k-1} | \Psi_o \rangle \tag{53}$$

holds if the basis set $\{|\phi_n\rangle\}$ satisfies

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

and

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i$$

and the function $u_k | \Psi_o \rangle$ is contained within the space spanned by the basis. Equation (53) may now be used to rewrite equations (43) and (44) in the form of the variational solution to the problem. The evaluation of $S(-t)$ for t even and t odd shall be dealt with separately. First examine $S(-t)$ for t even. From equation (44) it is known that

$$S(-t) = \langle \Psi_o | u_{\frac{t}{2}-1} u_{\frac{t}{2}} | \Psi_o \rangle.$$

Clearly if the variational basis contains $u_0 | \Psi_o \rangle$, $u_1 | \Psi_o \rangle$, ..., $u_{t/2} | \Psi_o \rangle$ then it follows that

$$S(-t) = \sum_m \langle \Psi_o | u_{\frac{t}{2}-1} | \phi_m \rangle \langle \phi_m | u_{\frac{t}{2}} | \Psi_o \rangle$$

$$= \sum_m 2 |\langle \phi_m | r \cos\theta | \Psi_o \rangle|^2 (\epsilon_m - E_o)^{1-t} \tag{54}$$

where the second line was obtained using equation (53) recursively. Similarly for t odd it is known from equation (43) that

$$S(-t) = \langle \Psi_o | u_{\frac{t-1}{2}}^2 | \Psi_o \rangle.$$

In this case if the variational basis contains $u_0 | \Psi_o \rangle$, $u_1 | \Psi_o \rangle$, ..., $u_{(t-1)/2} | \Psi_o \rangle$ it follows that

$$S(-t) = \sum_m \langle \Psi_0 | u_{\frac{t-1}{2}} | \phi_m \rangle \langle \phi_m | u_{\frac{t-1}{2}} | \Psi_0 \rangle$$

$$= \sum_m 2 |\langle \phi_m | r \cos\theta | \Psi_0 \rangle|^2 (\epsilon_m - E_0)^{1-t} \tag{55}$$

where again the second line was obtained using equation (53) recursively. Note that equations (54) and (55) are equal to the exact value of S(-t), yet they are also equal to the variational solution S'(-t) as given in equation (47). Therefore if the variational basis spans the space containing the functions listed above, the variational calculation will yield exact results.

Recalling that the form of u_k is given by equation (41) (for the ground state of atomic hydrogen) it is clear that if the variational basis spans a space containing the set of functions $r \cos\theta | \Psi_0 \rangle$, $r^2 \cos\theta | \Psi_0 \rangle$, ..., $r^n \cos\theta | \Psi_0 \rangle$ then the sums S(-1), S(-2), ..., S(-2n+1) will be satisfied exactly. S(0) will also be satisfied exactly due to the result of Dalgarno and Epstein[8] since the basis contains the $z | \Psi_0 \rangle$ term. Finally, if in addition the $\cos\theta | \Psi_0 \rangle$ term is included then S(1) and S(2) will also be satisfied, again due to the result of Dalgarno and Epstein (note that $\frac{\partial}{\partial z} | \Psi_0 \rangle = - \cos\theta | \Psi_0 \rangle$ for atomic hydrogen).

Bell[16] has examined, for the ground state of atomic hydrogen, the problem of sum rules for multipole operators of the form $r^j P_j(\cos\theta)$. Define $g_k^{(j)}(\vec{r})$ to be the solution of the equation

$$\Psi_0 \nabla^2 g_k^{(j)} + 2(\vec{\nabla}\Psi_0) \cdot (\vec{\nabla} g_k^{(j)}) = -g_{k-1}^{(j)} \tag{56}$$

and

$$g_0^{(j)} = 2^{\frac{1}{2}} r^j P_j(\cos\theta). \tag{57}$$

The solution may be shown to be of the form

$$g_k^{(j)}(\vec{r}) = r^j P_j(\cos\theta) h_k^{(j)}(r) \tag{58}$$

where

$$h_k^{(j)}(r) = \left(a_k^{(k,j)} r^k + a_{k-1}^{(k,j)} r^{k-1} + \cdots + a_0^{(k,j)} \right)$$ (59)

and $h_0^{(j)}(r) = 1$. As before with the dipole case, once the differential equation has been solved, the multipole oscillator strength sums may be obtained by evaluating

$$S(-t; r^j P_j(\cos\theta)) = \langle \Psi_0 | g_0^{(j)} g_{t-1}^{(j)} | \Psi_0 \rangle = \cdots = \langle \Psi_0 | (g_{\frac{t}{2}}^{(j)})^2 | \Psi_0 \rangle$$ (60)

for t odd, and

$$S(-t; r^j P_j(\cos\theta)) = \langle \Psi_0 | g_0^{(j)} g_{t-1}^{(j)} | \Psi_0 \rangle = \cdots = \langle \Psi_0 | g_{\frac{t}{2}-1}^{(j)} g_{\frac{t}{2}}^{(j)} | \Psi_0 \rangle$$ (61)

for t even.

The above results may now be used to determine the basis which allows multipole oscillator strength sums to be satisfied exactly. As usual, the variational basis is required to satisfy

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}$$

and

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} \epsilon_i .$$

Then the variational solution $S'(-t; r^j P_j(\cos\theta))$ to the multipole oscillator strength sum is given by

$$S'(-t; r^j P_j(\cos\theta)) = \sum_m 2 |\langle \phi_m | r^j P_j(\cos\theta) | \Psi_0 \rangle|^2 (\epsilon_m - E_0)^{1-t} .$$ (62)

Using arguments similar to those used for the dipole case it follows that if the variational basis spans a space containing the functions $r^j P_j(\cos\theta) | \Psi_0 \rangle$, $r^{j+1} P_j(\cos\theta) | \Psi_0 \rangle$, ..., $r^{j+m} P_j(\cos\theta) | \Psi_0 \rangle$ then the sum $S(k; r^j P_j(\cos\theta))$ will be satisfied exactly for k = -1, -2, ..., -2m-1. Certain of the sums $S(k; r^j P_j(\cos\theta))$ can be evaluated for k = 0, 1, 2, ... with techniques similar to those used for k = -1, -2, -3, ... The work of Lamm and Szabo[17] allows one to calculate $g_{-t}^{(j)}(\vec{r})$ for t = 1, 2, 3, ... using a recurrence procedure. Then the

multipole sums may be obtained by evaluating

$$S(t; r^j P_j (\cos\theta)) = \langle \psi_0 | (g^{(j)}_{-\frac{(t+1)}{2}})^2 | \psi_0 \rangle \tag{63}$$

for t odd, and

$$S(t; r^j P_j (\cos\theta)) = \langle \psi_0 | g^{(j)}_{-\frac{t}{2}} g^{(j)}_{-\frac{t}{2}-1} | \psi_0 \rangle . \tag{64}$$

In section E it shall be shown that the 2^j-pole oscillator strength for the ground state of hydrogen behaves asymptotically as $\epsilon^{-j-2.5}$ which implies $S(t; r^j P_j (\cos\theta))$ diverges at $t = j + 1.5$. Therefore evaluating equations (63) and (64) will lead to convergent results for $t = 0, 1, 2, \ldots, j+1$. For j odd the additional sums $S(t; r^j P_j (\cos\theta))$ for $t = 0, 1, 2, \ldots, j+1$ will be satisfied variationally if the basis spans a space which contains $P_j (\cos\theta) | \psi_0 \rangle$, $rP_j (\cos\theta) | \psi_0 \rangle$, $\ldots$, $r^j P_j (\cos\theta) | \psi_0 \rangle$. However for j even a subtlety involving the divergence of a matrix element occurs which prevents the $S(j+1; r^j P_j (\cos\theta))$ sum from being exactly obtainable from a variational basis. The remaining sums $S(t; r^j P_j (\cos\theta))$ for $t = 0$, 1, 2, $\ldots$, j may be obtained variationally if the basis spans a space containing $rP_j (\cos\theta) | \psi_0 \rangle$, $r^2 P_j (\cos\theta) | \psi_0 \rangle$, $\ldots$, $r^j P_j (\cos\theta) | \psi_0 \rangle$. Verification of these statements is quite straightforward.

E. MULTIPOLE OSCILLATOR STRENGTH DENSITY OF GROUND STATE - CONTINUUM TRANSITIONS FOR ONE ELECTRON ATOMS

The multipole oscillator strength density associated with a transition from the ground state to the continuum is sometimes useful for the evaluation of the summations over all states which arise in second order perturbation theory. The dipole oscillator strength is also required for the calculation of the photoionization cross section (in the dipole approximation) however the corrections from the higher order multipoles are usually not considered because in the high energy region where these corrections become important,

relativistic effects are also usually significant. The following discussion is concerned with the evaluation of the multipole oscillator strength density of the ground state - continuum transitions for one electron atoms. The derivation presented below is a generalization of the derivation for the dipole case contained in reference (9).

In order to compute the multipole oscillator strength density it is necessary to compute all matrix elements of the form

$$M_\ell = \langle u_{Wjm} | r^\ell Y_{\ell 0} | \Psi_0 \rangle \tag{65}$$

where Ψ_0 is the ground state wavefunction given by

$$\Psi_0 = Z^{\frac{3}{2}} \pi^{-\frac{1}{2}} e^{-Zr} \tag{66}$$

and u_{Wjm} is a continuum wavefunction (to be defined below). The Wigner-Eckart Theorem can be used to find that the above matrix element is nonzero only for $j = \ell$ and $m = 0$. Therefore it is necessary to consider only the continuum wavefunction[9] $u_{W\ell 0} = R_{W\ell} Y_{\ell 0}$ where

$$R_{W\ell} = (-)^{\ell+1} \frac{Z^{\frac{1}{2}}}{\sqrt{1-e^{-2\pi n'}}} \prod_{s=1}^{\ell} \sqrt{s^2+n'^2} \cdot (2kr)^{-(\ell+1)} \times$$

$$\times \frac{1}{\pi} \oint e^{-2ikr\xi} \left(\xi+\tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi-\tfrac{1}{2}\right)^{in'-\ell-1} d\xi \tag{67}$$

with $n' = Z/k$ and $k = (2\epsilon)^{1/2}$, and ϵ is the energy of $u_{W\ell 0}$.

Let $f(\xi)$ denote the integrand of the contour integral

$$f(\xi) = e^{-2ikr\xi} \left(\xi+\tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi-\tfrac{1}{2}\right)^{in'-\ell-1}. \tag{68}$$

The integrand $f(\xi)$ clearly contains branch points at $\xi = -1/2$ and $\xi = 1/2$. The branch cut is taken to lie between the two branch points, after defining a single valued branch by

$$f(\xi) = e^{-2ikr\rho_2 e^{i\phi_2}} \left(\rho_3 e^{i\phi_3}\right)^{-in'-\ell-1} \left(\rho_1 e^{i\phi_1}\right)^{in'-\ell-1}$$

$$= e^{-2ikr\rho_2 e^{i\phi_2}} \left(\rho_1 \rho_3 \right)^{-\ell-1} e^{-i(\ell+1)(\phi_1+\phi_3)} \times$$

$$\times e^{in'\ln(\rho_1/\rho_3)} e^{n'(\phi_3-\phi_1)} \tag{69}$$

where $\rho_1 = |\xi - 1/2|$, $\rho_2 = |\xi|$, $\rho_3 = |\xi + 1/2|$, $0 \le \phi_1 \le 2\pi$, $0 \le \phi_2 \le 2\pi$, $0 \le \phi_3 \le 2\pi$ with the angles measured as indicated in Figure 4.
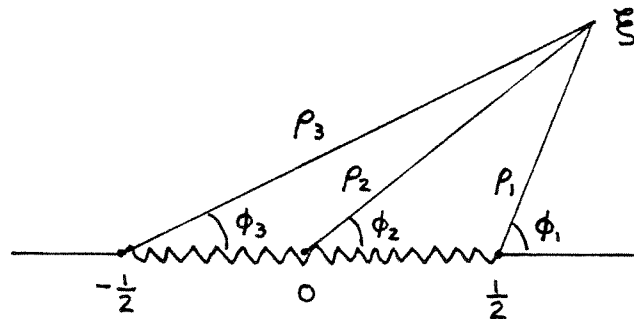

Figure 4

According to equation (69) the function $f(\xi)$ is analytic everywhere except on the real axis betwen $\xi = -1/2$ and $\xi = 1/2$. Finally, with this choice of the Riemann sheet the contour integral is evaluated along a path enclosing the branch cut as indicated in Figure 5.
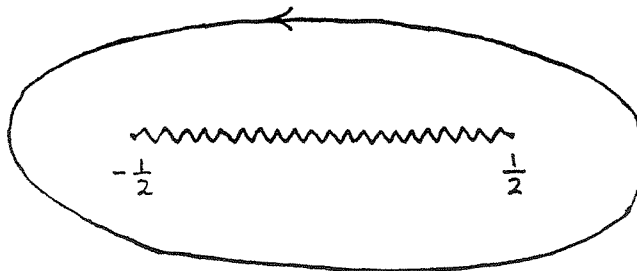

Figure 5

With the above definition for the continuum wave function it is now possible to evaluate the matrix element M_ℓ. The angular fac-

tors may be trivially integrated out using the orthonormality of the spherical harmonics, leaving only the radial integral remaining:

$$M_\ell = \int_0^\infty r^{\ell+2} R_{W\ell} \, \Psi_o \, dr$$

$$= (-)^{\ell+1} \frac{Z^2 \pi^{-\frac{3}{2}}}{\sqrt{1-e^{-2\pi n'}}} \prod_{s=1}^{\ell} \sqrt{s^2+n'^2} \times (2k)^{-(\ell+1)} \times$$

$$\times \int_0^\infty r \, e^{-Zr} \left\{ \oint e^{-2ikr\xi} \left(\xi+\tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi-\tfrac{1}{2}\right)^{in'-\ell-1} d\xi \right\} dr$$

$$= (-)^{\ell+1} \frac{Z^2 \pi^{-\frac{3}{2}}}{\sqrt{1-e^{-2\pi n'}}} \prod_{s=1}^{\ell} \sqrt{s^2+n'^2} \times (2k)^{-(\ell+1)} \times$$

$$\times \int_0^\infty \left\{ \oint r \, e^{-(Z+2ik\xi)r} \left(\xi+\tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi-\tfrac{1}{2}\right)^{in'-\ell-1} d\xi \right\} dr$$

$$= (-)^{\ell+1} \frac{Z^2 \pi^{-\frac{3}{2}}}{\sqrt{1-e^{-2\pi n'}}} \prod_{s=1}^{\ell} \sqrt{s^2+n'^2} \times (2k)^{-(\ell+1)} \times J \qquad (70)$$

where

$$J = \int_0^\infty \left\{ \oint r \, e^{-(Z+2ik\xi)r} \left(\xi+\tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi-\tfrac{1}{2}\right)^{in'-\ell-1} d\xi \right\} dr \, . \qquad (71)$$

At this point it is necessary to interchange the radial integral with the contour integral, however this interchange can only be effected if the imaginary part of ξ is less than $Z/(2k)$, otherwise the radial integration will yield a meaningless (i.e. divergent) result. Prior to this step the contour could trace anywhere around the branch cut, but to interchange the order of integration it is necessary to first deform the contour such that it does not lie above $\xi = Zi/(2k)$. Of course deforming the contour (without crossing singularities) cannot affect the value of the original contour integral (as a consequence of Cauchy's Theorem). After making this restriction on the path of integration one obtains

$$J = \oint \left\{ \int_0^\infty r\, e^{-(Z+2ik\xi)r}\, dr \right\} \left(\xi + \tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi - \tfrac{1}{2}\right)^{in'-\ell-1} d\xi$$

$$= \oint \frac{\left(\xi + \tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi - \tfrac{1}{2}\right)^{in'-\ell-1}}{(Z + 2ik\xi)^2}\, d\xi$$

$$= \frac{-1}{4k^2} \oint \frac{\left(\xi + \tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi - \tfrac{1}{2}\right)^{in'-\ell-1}}{\left(\xi - \tfrac{Z}{2k}i\right)^2}\, d\xi \qquad (72)$$

Notice the radial integration has introduced a second order pole located at ξ = Zi/(2k). The above discussion concerning the integration path implies that the pole is located outside the contour as indicated in Figure 6.
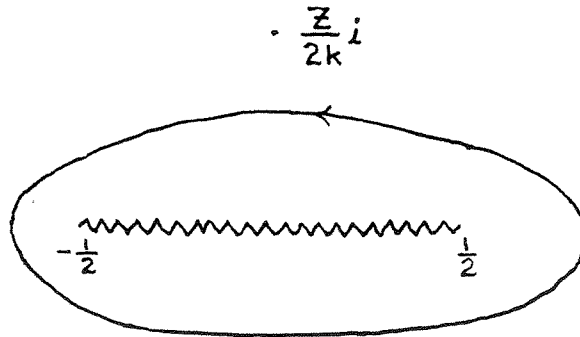

Figure 6

As shown in Figure 6 the contour integral does not lend itself to simple computation but this situation may be remedied by deforming the contour as in Figure 7. Note that the integrand behaves asymptotically as $\xi^{-2\ell-4}$ for large ξ and the ℓ of interest range over only the positive integers. The large circle is taken at infinity so it yields no contribution (because of the $\xi^{-2\ell-4}$ behavior) and the paths connecting the circle around the pole to the circle at infinity give equal and opposite contributions. Therefore the integral over the path in Figure 7 yields the same value as the in-
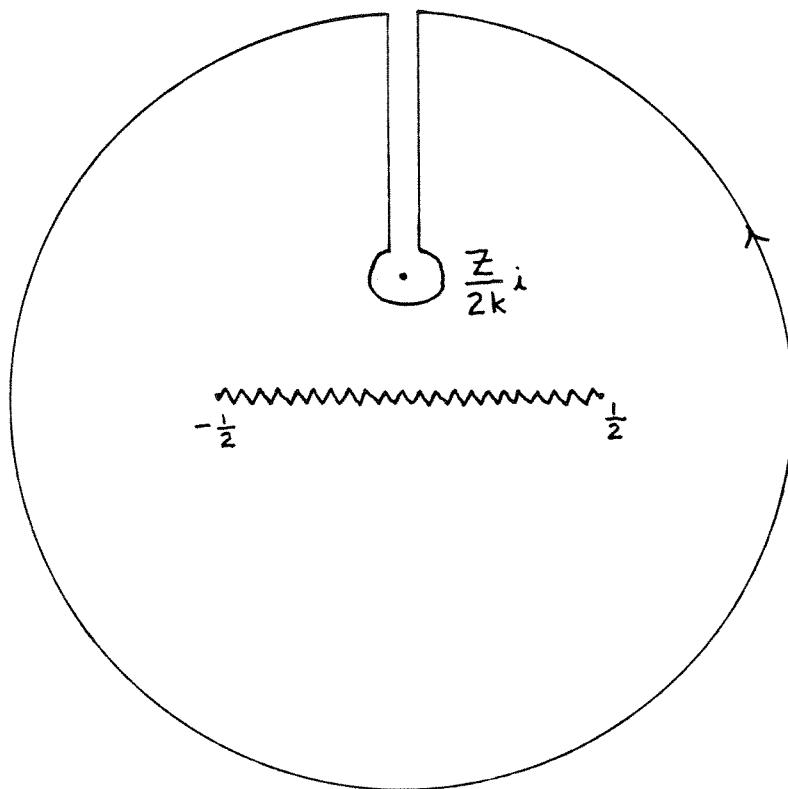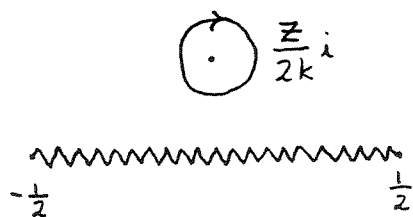
Figure 7

tegral over the path shown in Figure 8.

Figure 8

The integration path in Figure 8 is such that the integral may be readily evaluated using the residue theorem as follows.

$$J = -2\pi i \frac{d}{d\xi} \left[\frac{-1}{4k^2} \left(\xi + \tfrac{1}{2}\right)^{-in'-\ell-1} \left(\xi - \tfrac{1}{2}\right)^{in'-\ell-1} \right] \Bigg|_{\xi = \frac{1}{2}in'}$$

$$= (-)^\ell \frac{2^{2\ell+3}\pi \ell n'}{k^2(n'^2+1)^{\ell+2}} \left(\frac{in'-1}{in'+1}\right)^{in'}$$

$$= (-)^\ell \frac{2^{2\ell+3}\pi \ell n'}{k^2(n'^2+1)^{\ell+2}} \, e^{-2n'\,\mathrm{arccot}\,n'} \tag{73}$$

where the last step was performed by using the identity

$$z = \tan\left[\frac{i}{2}\ln\left(\frac{i+z}{i-z}\right)\right] \tag{74}$$

which can readily be verified by expanding the tangent in terms of exponentials. Replacing J in equation (70) by the result obtained in equation (75) yields the value of the matrix element

$$M_\ell = -Z^3\pi^{-\frac{1}{2}} \frac{2^{\ell+2}\ell}{k^{\ell+4}(n'^2+1)^{\ell+2}} \frac{e^{-2n'\,\mathrm{arccot}\,n'}}{\sqrt{1 - e^{-2\pi n'}}} \times$$

$$\times \prod_{s=1}^{\ell} \sqrt{s^2 + n'^2} \tag{75}$$

Finally the value of the multipole oscillator strength density is given by

$$\frac{df_{100,\epsilon\ell 0}\left(r^\ell Y_{\ell 0}\right)}{d\epsilon} = 2\left|M_\ell\right|^2 (\epsilon - E_0) \tag{76}$$

and here $E_0 = -Z^2/2$, therefore

$$\frac{df_{100,\epsilon\ell 0}\left(r^\ell Y_{\ell 0}\right)}{d\epsilon}$$

$$= \frac{Z^6}{\pi}\ \frac{2^{2\ell+5}\ \ell^2}{k^{2\ell+8}\left(n'^2+1\right)^{2\ell+4}}\ \frac{e^{-4n'\,\mathrm{arccot}\,n'}}{1-e^{-2\pi n'}}\ \times$$

$$\times \left(\prod_{s=1}^{\ell}\left(s^2+n'^2\right)\right) \times \left(\epsilon+\frac{Z^2}{2}\right)$$

$$= \frac{Z^6}{\pi}\ \frac{2^{\ell+1}\ \ell^2}{\epsilon^{\ell+4}\left(n'^2+1\right)^{2\ell+4}}\ \frac{e^{-4n'\,\mathrm{arccot}\,n'}}{1-e^{-2\pi n'}}\ \times$$

$$\times \left(\prod_{s=1}^{\ell}\left(s^2+n'^2\right)\right) \times \left(\epsilon+\frac{Z^2}{2}\right) \tag{77}$$

where n' = $Z/(2\epsilon)^{1/2}$. The above equation for the operator $r^\ell Y_{\ell 0}$ may be rewritten as an equation for the operator $r^\ell P_\ell(\cos\theta)$ by using the identity

$$Y_{\ell 0}(\theta,\phi) = \left(\frac{2\ell+1}{4\pi}\right)^{\frac{1}{2}} P_\ell(\cos\theta) \tag{78}$$

therefore

$$\frac{df_{100,\epsilon\ell 0}\left(r^\ell P_\ell(\cos\theta)\right)}{d\epsilon}$$

$$= \frac{Z^6}{(2\ell+1)}\ \frac{2^{\ell+3}\ \ell^2}{\epsilon^{\ell+4}\left(n'^2+1\right)^{2\ell+4}}\ \frac{e^{-4n'\,\mathrm{arccot}\,n'}}{1-e^{-2\pi n'}}\ \times$$

$$\times \left(\prod_{s=1}^{\ell}\left(s^2+n'^2\right)\right)\left(\epsilon+\frac{Z^2}{2}\right) \tag{79}$$

The asymptotic behavior of equation (79) is of interest for various reasons, including the determination of the argument k at which the multipole oscillator strength sum $S(k;r^\ell P_\ell(\cos\theta))$ diverges. The

first two asymptotic terms may be obtained by a straightforward expansion of equation (79):

$$\frac{df_{100,\epsilon\ell 0}\left(r^\ell P_\ell(\cos\theta)\right)}{d\epsilon}$$

$$\cong \frac{Z^6}{(2\ell+1)} \; \frac{2^{\ell+3}\ell^2}{\epsilon^{\ell+3}} \; \frac{1-\pi n'}{2\pi n'}\left(\prod_{s=1}^{\ell} s\right)^2$$

$$\cong \frac{Z^5}{(2\ell+1)} \; \frac{2^{\ell+2}\sqrt{2}}{\pi}\left(\prod_{s=1}^{\ell} s\right)^2 \frac{1-\pi Z(2\epsilon)^{-\frac{1}{2}}}{\epsilon^{\ell+2.5}} \qquad . \tag{80}$$

Therefore the asymptotic behavior of the 2^ℓ-pole oscillator strength density is seen to behave as

$$\frac{df_{100,\epsilon\ell 0}\left(r^\ell P_\ell(\cos\theta)\right)}{d\epsilon} \;\propto\; \epsilon^{-\ell-2.5} \qquad . \tag{81}$$

F. APPLICATIONS OF MULTIPOLE OSCILLATOR STRENGTHS TO STATIC ELECTRIC INTERACTION PROBLEMS

For practical purposes the multipole expansions discussed in Section C are of interest only up to quadrupole order (or at most, up to octupole order). Beyond this order the higher terms usually yield corrections which are physically insignificant and if this is not the case the applicability of the expansion is questionable. In this section the evaluation of perturbation expressions shall be discussed for when multipole expansions are taken to this order.

The simplest interaction where the multipole expansion is of interest is that of an atom or molecule in a static electric field. The perturbation to the unperturbed Hamiltonian is equal to

$$\sum_{i=1}^{N} e_i \, \phi(\vec{r}_i)$$

where $\phi(\vec{r})$ is the scalar potenetial due to fixed external charges. Assuming $\phi(\vec{r})$ is being considered over a localized region which does not contain the fixed external charges, it satisfies Laplace's equation

$$\nabla^2 \phi(\vec{r}) = 0$$

which for this situation has the general solution given by

$$\phi(\vec{r}) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} A_{\ell m} r^\ell Y_{\ell m}(\theta, \phi) . \tag{82}$$

The $\ell = 0$ contribution may be ignored since only the gradient of the potential is of physical significance. Truncating the series after the quadrupole term leads to

$$\phi(\vec{r}) = \sum_{\ell=1}^{2} \sum_{m=-\ell}^{\ell} A_{\ell m} r^\ell Y_{\ell m}(\theta, \phi) . \tag{83}$$

The coefficients A_{1m} may be related to the cartesian components F_α of the electric field vector by solving the system of equations

$$\frac{\partial \phi}{\partial x_\alpha} = -F_\alpha \qquad \alpha = 1,3 . \tag{84}$$

Similarly the coefficients A_{2m} may be related to the cartesian components $F_{\alpha\beta}$ of the electric field gradient tensor by solving the system of equations

$$\frac{\partial^2 \phi}{\partial x_\alpha \partial x_\beta} = -F_{\alpha\beta} \qquad \alpha, \beta = 1,3 . \tag{85}$$

Of the above nine equations, only five are independent since $F_{\alpha\beta}$ is a traceless (as a consequence of Laplace's equation), symmetric tensor hence the determination of the five A_{2m}'s is a well posed problem. Note that since ϕ in equation (83) may be written as a second

order polynomial in the x_α's, Taylor's Theorem allows the potential to be written in the cartesian form

$$\phi(\vec{r}) = -F_\alpha x_\alpha - \frac{1}{2} F_{\alpha\beta} x_\alpha x_\beta$$

$$= -F_\alpha x_\alpha - \frac{1}{2}\left(x_\alpha x_\beta - \frac{1}{3} r^2 \delta_{\alpha\beta}\right) F_{\alpha\beta} \tag{86}$$

where the summation convention has been taken. The second line follows from the fact that $F_{\alpha\beta} \delta_{\alpha\beta} = 0$ is the definition that $F_{\alpha\beta}$ is a traceless tensor and the $(1/3)r^2$ factor has been chosen such that $(x_\alpha x_\beta - (1/3)r^2 \delta_{\alpha\beta})$ is itself a traceless tensor.

Classically, the Hamiltonian for the interaction of localized charges with a potential ϕ (due to external fixed charges) is given by

$$H = H_0 + \sum_i e_i \phi(\vec{r}_i) \tag{87}$$

$$= H_0 + H' \tag{88}$$

where

$$H' = -\mu_\alpha F_\alpha - \Theta_{\alpha\beta} F_{\alpha\beta} \tag{89}$$

with dipole moment tensor

$$\mu_\alpha = \sum_i e_i x_{i\alpha} \tag{90}$$

and quadrupole moment tensor

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_i e_i \left(x_{i\alpha} x_{i\beta} - \frac{1}{3} r_i^2 \delta_{\alpha\beta} \right). \tag{91}$$

Quantum Mechanically, the expectation values of the dipole and quadrupole moment tensors for an eigenstate $|\psi\rangle$ of the full Hamiltonian $H = H_0 + H'$ are given by

$$\langle \mu_\alpha \rangle = \langle \psi | \sum_i e_i x_{i\alpha} | \psi \rangle \tag{92}$$

and

$$\langle \Theta_{\alpha\beta} \rangle = \langle \psi | \frac{1}{2} \sum_i e_i (x_{i\alpha} x_{i\beta} - \frac{1}{3} r_i^2 \delta_{\alpha\beta}) | \psi \rangle . \tag{93}$$

The standard approach to calculating these expectation values is to use a perturbative expansion. The nth order perturbation wavefunction $| \psi^{(n)} \rangle$ is valid to the nth power of the perturbation parameter. Since the perturbation wavefunctions need not be normalized the nth order approximations to the expectation values must be calculated according to

$$\langle \mu_\alpha^{(n)} \rangle = \frac{\langle \psi^{(n)} | \sum_i e_i x_i | \psi^{(n)} \rangle}{\langle \psi^{(n)} | \psi^{(n)} \rangle} \tag{94}$$

and

$$\langle \Theta_{\alpha\beta}^{(n)} \rangle = \frac{\langle \psi^{(n)} | \frac{1}{2} \sum_i e_i (x_{i\alpha} x_{i\beta} - \frac{1}{3} r_i^2 \delta_{\alpha\beta}) | \psi^{(n)} \rangle}{\langle \psi^{(n)} | \psi^{(n)} \rangle} \tag{95} .$$

A somewhat more convenient method for calculating $\langle \mu_\alpha^{(n)} \rangle$ and $\langle \Theta_{\alpha\beta}^{(n)} \rangle$ has been given by Buckingham[18]. Classically, the dipole and quadrupole moment tensors are equal to minus the partial derivative of the Hamiltonian with respect to the appropriate field parameter, i.e.

$$\mu_\alpha = \frac{-\partial H}{\partial F_\alpha} \tag{96}$$

and

$$\Theta_{\alpha\beta} = \frac{-\partial H}{\partial F_{\alpha\beta}} \tag{97} .$$

Quantum Mechanically the relations analogous to equations (96) and (97) are

$$\langle \mu_\alpha \rangle = -\frac{\partial E}{\partial F_\alpha} \qquad (98)$$

and

$$\langle \Theta_{\alpha\beta} \rangle = -\frac{\partial E}{\partial F_{\alpha\beta}} \qquad (99)$$

where E is the energy for the eigenstate $|\psi\rangle$ of the full Hamiltonian (i.e. $(H_0 + H')|\psi\rangle = E|\psi\rangle$) which has been reached adiabatically from the unperturbed eigenstate. Note that the nth order perturbation wavefunction $|\psi^{(n)}\rangle$ may be used to calculate the n+1 order energy through the relation

$$E^{(n+1)} = \frac{\langle \psi^{(n)} | H_o + H' | \psi^{(n)} \rangle}{\langle \psi^{(n)} | \psi^{(n)} \rangle} \qquad (100)$$

The extra order of accuracy achieved is a consequence of the orthogonality of the unperturbed wavefunction with the perturbative corrections. Hence, $\langle \mu_\alpha^{(n)} \rangle$ and $\langle \Theta_{\alpha\beta}^{(n)} \rangle$ may also be computed from

$$\langle \mu_\alpha^{(n)} \rangle = -\frac{\partial E^{(n+1)}}{\partial F_\alpha} \qquad (101)$$

and

$$\langle \Theta_{\alpha\beta}^{(n)} \rangle = -\frac{\partial E^{(n+1)}}{\partial F_{\alpha\beta}} \qquad (102)$$

The following treatment examines the case where the unperturbed state under consideration is nondegenerate. The degenerate case may be treated similarly by using the more general perturbative expansions for the energy and the wavefunctions listed by Condon and Shortley[19]. The perturbative expansions of $\langle \mu_\alpha \rangle$ and $\langle \Theta_{\alpha\beta} \rangle$ shall be computed up to third order, which requires the fourth order expansion of the energy, $E^{(4)}$. Morse and Feshbach[20] have given a simple formula for obtaining approximate expressions for energies and wavefunctions valid to the nth power of the perturbation parameter. Using this

technique to obtain $E^{(4)}$ it is found that

$$E^{(4)}$$

$$= E_0 + \langle 0|H'|0\rangle$$

$$+ \sum_{m\neq 0} \frac{|\langle m|H'|0\rangle|^2}{E_0 + \langle 0|H'|0\rangle + \sum_{n\neq 0}\frac{|\langle n|H|0\rangle|^2}{E_n - E_0} - E_m}$$

$$+ \sum_{\substack{m\neq 0 \\ n\neq 0}} \frac{\langle 0|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|0\rangle}{\left(E_0+\langle 0|H'|0\rangle - E_m\right)\left(E_0+\langle 0|H'|0\rangle - E_n\right)}$$

$$+ \sum_{\substack{m\neq 0 \\ n\neq 0 \\ p\neq 0}} \frac{\langle 0|H'|p\rangle\langle p|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|0\rangle}{\left(E_0-E_m\right)\left(E_0-E_n\right)\left(E_0-E_p\right)} \qquad (103)$$

The perturbation matrix elements in the denominators are small compared with the energy differences, hence may be eliminated from the denominators by a simple expansion, which leads to

$$E^{(4)}$$

$$= E_0 + \langle 0|H'|0\rangle + \sum_{m\neq 0} \frac{|\langle m|H'|0\rangle|^2}{E_0 - E_m}$$

$$+ \sum_{\substack{m\neq 0 \\ n\neq 0}} \frac{\langle 0|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|0\rangle}{\left(E_0-E_m\right)\left(E_0-E_n\right)} - \sum_{m\neq 0} \frac{|\langle m|H'|0\rangle|^2\langle 0|H'|0\rangle}{\left(E_0-E_m\right)^2}$$

$$+ \sum_{\substack{m\neq 0 \\ n\neq 0 \\ p\neq 0}} \frac{\langle 0|H'|p\rangle\langle p|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|0\rangle}{\left(E_0-E_m\right)\left(E_0-E_n\right)\left(E_0-E_p\right)} + \sum_{m\neq 0} \frac{|\langle m|H'|0\rangle|^2|\langle 0|H'|0\rangle|^2}{\left(E_0-E_m\right)^3}$$

$$- \sum_{\substack{m\neq 0 \\ n\neq 0}} \frac{|\langle n|H'|0\rangle|^2|\langle m|H'|0\rangle|^2}{\left(E_0-E_m\right)^2\left(E_0-E_n\right)} - 2\sum_{\substack{m\neq 0 \\ n\neq 0}} \frac{\langle 0|H'|n\rangle\langle n|H'|m\rangle\langle m|H'|0\rangle\langle 0|H'|0\rangle}{\left(E_0-E_m\right)^2\left(E_0-E_n\right)} \qquad (104)$$