

Sum Rules and Atomic Structure

A. DALGARNO*

Geophysics Corporation of America, Bedford, Massachusetts

1. INTRODUCTION

LET ψ_s be the s th eigenfunction of the Hamiltonian H of some physical system and let E_s be the corresponding eigenvalue. Let p and q be operators. Infinite summations of matrix elements

$$S_k = \mathbf{S}'_{s \neq i} (E_i - E_s)^k (\psi_i, p\psi_s) (\psi_s, q\psi_i) \quad (1)$$

occur frequently in quantum mechanics and it is the purpose of this paper to draw attention to the fact that S_k can be evaluated directly for all integer values of k , both positive and negative, from a knowledge of either ψ_i or ψ_f .

2. THEORY

We define the more general summation

$$S_k = \mathbf{S}'_{s \neq i} (E_i - E_s)^k (\psi_i, p\psi_s) (\psi_s, q\Psi), \quad (2)$$

where Ψ is any eigenfunction and need not belong to the complete set of eigenfunctions ψ_s of H . For simplicity of presentation, we suppose that all quantities are real. There are several ways by which the formal evaluation of S_k can be achieved. Perhaps the most flexible and most simple procedure is that employed by Dalgarno and Lewis¹ which is based upon the obvious identity

$$(\psi_s, p\psi_i) = \frac{(\psi_s, [E_i - H]^k p\psi_i)}{(E_i - E_s)^k}. \quad (3)$$

It follows immediately that

$$S_k = ([E_i - H]^k (p\psi_i), q\Psi). \quad (4)$$

Specializing to the case when $\Psi = \psi_i$, (4) becomes

$$S_k = ([E_i - H]^k (p\psi_i), q\psi_i) \quad (5)$$

or, equivalently,

$$S_k = ([E_i - H]^{k-t} (p\psi_i), [E_i - H]^t (q\psi_i)), \quad 0 \leq t \leq k. \quad (6)$$

Various special forms of (5) and (6) for the case in

*On leave from Department of Applied Mathematics, Queens University of Belfast, Northern Ireland.

¹A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) **A233**, 70 (1955); A. Dalgarno and A. L. Stewart, *ibid.* **A238**, 269 (1956).

which $q = p$, so that

$$S_k = \mathbf{S}'_{s \neq i} (E_i - E_s)^k |(\psi_i, p\psi_s)|^2, \quad (7)$$

have appeared in the literature.²

Formula (4) can also be used for negative values of k . We introduce the functions χ_n such that

$$(H - E_i)\chi_n + \chi_{n-1} = 0, \quad (8)$$

where

$$\chi_0 = \{p - (\psi_i, p\psi_i)\}\psi_i. \quad (9)$$

Then

$$(\chi_{n-1}, \psi_i) = 0, \quad (10)$$

and

$$S_k = (\chi_{|k|}, q\Psi). \quad (11)$$

If $\Psi = \psi_i$, (11) becomes

$$S_k = (\chi_{|k|}, q\psi_i), \quad (12)$$

or, equivalently,

$$S_k = (\chi_{|k|-t}, \chi'_t), \quad 0 \leq t \leq |k|, \quad (13)$$

where

$$(H - E_i)\chi'_n + \chi'_{n-1} = 0, \quad (14)$$

such that

$$\chi'_0 = \{q - (\psi_i, q\psi_i)\}\psi_i, \quad (15)$$

and

$$(\chi'_{n-1}, \psi_i) = 0. \quad (16)$$

An alternative procedure for evaluating S_k for negative values of k may be more convenient. Let $\chi(\omega)$ be the solution of the equation

$$(H - E_i - \omega)\chi(\omega) + \{p - (\psi_i, p\psi_i)\}\psi_i = 0, \quad (17)$$

such that

$$(\psi_i, \chi(\omega)) = 0. \quad (18)$$

Then

$$S_{-1}(\omega) = \mathbf{S}'_{s \neq i} \frac{(\psi_i, p\psi_s) (\psi_s, q\Psi)}{(E_i - E_s + \omega)} \quad (19)$$

²J. P. Vinti, Phys. Rev. **41**, 432 (1932); A. Dalgarno and N. Lynn, Proc. Phys. Soc. (London) **A70**, 802 (1957); K. K. Rebane, Opt. Spectr. **9**, 295 (1960); O. I. Sil'd, *ibid.* **11**, 75 (1961); K. K. Rebane and O. I. Sil'd, *ibid.* **13**, 259 (1962).

can be written simply as^{3,4}

$$S_{-1}(\omega) = (\chi(\omega), q\Psi), \quad (20)$$

and the summations (2) for negative values of k can be identified with the derivatives of $S_{-1}(\omega)$ evaluated at $\omega = 0$ by the relation

$$S_k = \frac{(-1)^{k-1}}{(|k| - 1)!} \frac{d^{|k|-1}}{d\omega^{|k|-1}} S_{-1}(\omega = 0). \quad (21)$$

This development is closely related to the early work of Podolsky.⁵

By ingenious use of Laplace transform techniques, Schwartz and Tieman^{3,6} have calculated (19) for the case when $p = q$ is the position vector \mathbf{r} of the electron and $\Psi = \psi_i$ is an eigenfunction of the hydrogen atom, and some solutions of (8) have been reported for the case $p = \mathbf{r}$.⁷ For more complex systems, it is necessary to use variational techniques. Equation (8) can be solved by minimizing the functional

$$J_n = (\chi_n | H - E_i | \chi_n) + 2(\chi_n, \chi_{n-1}) \quad (22)$$

with respect to a selected trial function χ_n , and (17) can be solved by minimizing the functional

$$J(\omega) = (\chi(\omega) | H - E_i - \omega | \chi(\omega)) + 2(\chi(\omega) | p - (\psi_i, p\psi_i) | \psi_i). \quad (23)$$

Schwartz⁸ has used (23) to calculate the Lamb shift in helium but the computational labor is formidable and a simple procedure is necessary for heavier atoms and for molecules. It is natural to seek an extension of the Hartree-Fock approximation.

3. THE HARTREE-FOCK SCHEME

The extension of the Hartree-Fock scheme to the evaluation of infinite summations (2) follows from the recognition that Eq. (8) with $n = 1$:

$$(H - E_i)\chi + \{p - (\psi_i, p\psi_i)\}\psi_i = 0 \quad (24)$$

is the equation for the first-order perturbed wave function resulting from the application of a perturbing potential p to the system described by ψ_i . The extension of the Hartree-Fock scheme to perturbed

atomic systems is straightforward and has been written out explicitly for the case when p is a sum of one-electron operators.^{9,10} There are two possible extensions, the uncoupled approximation and the coupled approximation,¹¹ of which the former is easier and the latter more accurate.⁹ They may be applied systematically to the solution of (8) by regarding (χ_{n-1}/ψ_i) as a perturbation.

Except for helium, the form of the perturbation becomes complicated as n increases. This increasing complexity can be avoided, though with some loss of accuracy, by solving (8) with the restriction that

$$\chi_n = \{f_n(\mathbf{r}_1) + f_n(\mathbf{r}_2) + \dots\}\psi_i, \quad (25)$$

the \mathbf{r}_i being the position vectors of the electrons. The resulting equation for $f_n(\mathbf{r})$ is usually easy to solve. A similar technique has been used by Pople and Schofield¹² to solve the first-order perturbed equation (24) appropriate to the dipole polarization of argon.

It should be possible to develop systematic methods for solving (8) also when ψ_i is represented by the Thomas-Fermi model.

4. VAN DER WAALS COEFFICIENTS

Sum rules provide a means of limiting the error in calculations which involve summations which are similar to but not identical with (2). Thus, the leading term of the interaction potential at large separations r of a pair of neutral atoms a and b in nondegenerate states with eigenfunctions ψ_a^0 and ψ_b^0 , respectively, is $-C/r^6$, and C may be written¹³ in atomic units as

$$C = 12 \sum_{s \neq 0} \sum_{t \neq 0} \frac{f_a^s f_b^t}{(E_a^s - E_a^0)(E_b^t - E_b^0)(E_a^s + E_b^t - E_a^0 - E_b^0)}, \quad (26)$$

where f^s is the oscillator strength of the electric dipole transition from state 0 to state s

$$f^s = \frac{1}{3} (E^s - E^0) |(\psi^0, \sum_j \mathbf{r}_j \psi^s)|^2, \quad (27)$$

and E^s and ψ^s are, respectively, the eigenvalue and eigenfunction of the s th state.

Summations of the form (7) with $p = \sum_j \mathbf{r}_j$ have been evaluated for a number of systems using the-

³ C. Schwartz and J. J. Tieman, *Ann. Phys.* **2**, 178 (1959).

⁴ A. Dalgarno, *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1961), Vol. 1.

⁵ B. Podolsky, *Proc. Natl. Acad. Sci.* **4**, 253 (1928).

⁶ The solution for the ground state has been used recently by M. H. Mittleman and F. A. Wolf [*Phys. Rev.* **128**, 2686 (1962)] in a computation of the scattering of light. This calculation supercedes the earlier values of references 5 and 7.

⁷ A. Dalgarno and A. E. Kingston, *Proc. Roy. Soc. (London)* **A259**, 424 (1960).

⁸ C. Schwartz, *Phys. Rev.* **123**, 1700 (1961).

⁹ A. Dalgarno, *Proc. Roy. Soc. (London)* **A251**, 282 (1959).

¹⁰ S. Kaneko, *J. Phys. Soc. Japan* **14**, 1600 (1959); L. E. Allen, *Phys. Rev.* **118**, 167 (1960).

¹¹ A. Dalgarno, *Advan. Phys.*, **11**, 282 (1962).

¹² J. A. Pople and P. Schofield, *Phil. Mag.* **2**, 591 (1957).

¹³ H. Margenau, *Rev. Mod. Phys.* **11**, 1 (1939).

oretical calculations and using experimental data on polarizabilities, refractive indices, and Verdet constants.¹⁴ There are available also theoretical and measured values of some of the oscillator strengths occurring in (26). To calculate C , the available oscillator strengths were extended and modified in such a way that a large number of sum rules were exactly satisfied. It was ensured, in particular, that the derived oscillator strengths yielded S_{-1} accurately since the form of (26) is similar to the product of two such summations. The resulting accuracy is largely determined by the accuracy with which S_{-1} is known, S_{-1} being essentially the dipole polarizability. In none of the cases given in Table I¹⁴ should the error exceed 20% and it is usually very much less.

¹⁴ A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. (London) **A73**, 455 (1959); **78**, 607 (1961); A. Dalgarno and D.A. Williams (unpublished).

TABLE I. Values of van der Waals coefficients C in atomic units.^{a,b}

	H	He	Ne	Ar	H ₂ ^c
H	6.5	2.8	5.7	20.2	9.2
He	2.8	1.5	3.1	9.9	4.2
Ne	5.7	3.1	6.6	20.6	8.6
Ar	20.2	9.9	20.6	68.1	29.6
H ₂ ^c	9.2	4.2	8.6	29.6	13.3
Li	67	22	48	200	88
Na	74	25	52	210	96
K	99	33	68	280	128
Rb	100	34	69	280	132
Cs	120	38	77	320	148

^a The interaction energy is $[-C/(r/a_0)^6][e^2/a_0]$, a_0 being the Bohr radius.
^b Values for additional systems are given in the references. (See reference 14.)

^c The H₂ values are averages over all orientations.

ACKNOWLEDGMENT

I am indebted to Professor J. O. Hirschfelder for encouraging me to present this account of summation techniques.

Sensitivity of $L_1L_{2,3}M_{4,5}$ Coster-Kronig Transition Rates to Variations in Energy Levels and Screening Parameters

EDWIN J. CALLAN

Aeronautical Research Laboratories, Wright-Patterson Air Force Base, Ohio

STUDY of the $L_1L_{2,3}M_{4,5}$ Coster-Kronig transition rates offers a sensitive tool for comparisons of various atomic wave functions. These transitions are sensitive to different screening parameters arising from use of different wave function computations and also have pointed up several inconsistencies in tabulated energy-level values. While there are many transitions of the Coster-Kronig type,¹⁻³ the $L_1L_{2,3}M_{4,5}$ have the features of large transition rates, sharp cutoffs at various atomic numbers, and greater proportion of the very scanty data on such transitions.

This class of transition, first described by Coster and Kronig in 1935,¹ is distinguished by the filling of a deep vacancy in an atom by another electron of the same shell, but different subshell, with ejection of another electron of different shell with low energy. The final doubly ionized state serves as the initial state for emission of x-ray satellite lines of relatively

high intensity, relative to the parent lines. Because of the nature of the variations of energy levels with atomic number, these transitions are energetically possible only for certain regions of atomic number.²⁻⁴ The general features of these transitions and their consequences have been reviewed by Burhop³ and more recently by Listengarten.⁴ The current work is concerned only with the $L_1L_{2,3}M_{4,5}$ transitions, hereafter called LLM transitions. Only a few previous calculations have been made of transition rates for the LLM transitions, including those of Ramberg and Richtmyer⁵ for Au, based on the Thomas-Fermi field, of Pincherle⁶ using hydrogenic functions, and of Rubinstein and Snyder⁷ using a SCF function for Kr. The present calculations cover the atomic number region from Sc to Sn.

⁴ M. A. Listengarten, Izv. Akad. Nauk SSSR, Ser. Fiz., **24**, 1041 (1960).

⁵ E. Ramberg and F. Richtmyer, Phys. Rev. **51**, 913 (1937).

⁶ L. Pincherle, Nuovo Cimento **12**, 81 (1935).

⁷ R. A. Rubinstein and J. N. Snyder, Phys. Rev. **97**, 1653 (1955); also R. A. Rubinstein, thesis, University of Illinois, 1955 (unpublished).

¹ D. Coster and R. Kronig, Physica **2**, 13 (1935).

² J. N. Cooper, Phys. Rev. **65**, 155 (1944).

³ E. H. S. Burhop, *The Auger Effect and Other Radiationless Transitions* (Cambridge University Press, New York, 1952).