and lower bounds to van der Waals coefficients.

[5]It is easy to see that if each of the factors in the integrand of (8) is replaced by $\chi(\omega)$, where $\chi(\omega)=\frac{1}{2}[P(\omega+W_1+i\delta)+P(-\omega+W_1+i\delta)]$, the integral is unchanged. On deforming the (Feynman-type) ω contour to run along the imaginary axis and using $\chi(\omega)=\chi(-\omega)$, we get $C_{HH}\propto\int_0^\infty\chi^2(i\omega)d\omega$, which is the form used by many authors [$\chi(\omega)\propto\alpha(\omega)$, the dynamic polarizability].

[6]J. Schwinger, J. Math. Phys. 5, 1606 (1964). Other forms are given by E. H. Wichmann and C. H. Woo, J. Math. Phys. 2, 178 (1961), and L. Hostler, J. Math. Phys. 5, 591 (1964).

[7]Higher Transcendental Functions, Bateman Manuscript Project (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 1, p. 114, Eq. 3.

[8]After this work was completed we discovered that a representation for $P(E)$ similar to (11) had been obtained by M. Karplus and H. J. Kolker [J. Chem. Phys. 39, 1493 (1963)], by use of a different method; the connection of their representation with hypergeometric functions may be inferred by a scale change in the integration variable. We have also learned that our method for computing $P(E)$ is essentially the same as that used by M. Gavrila [Phys. Rev. 163, 147 (1967)] in the evaluation of an integral closely related to (9). That an exact calculation of C_{HH} should be possible has also been noted by A. Dalgarno, Advan. Chem. Phys. 12, 143 (1967).

[9]We refer here only to those higher inverse powers arising from the higher multipoles in the electrostatic interaction. For recent discussions of the asymptotic behavior of the interaction potential for large R, see G. Feinberg and J. Sucher, J. Chem. Phys. 48, 3333 (1968), and references given there.

MINIMA OF GENERALIZED OSCILLATOR STRENGTHS*

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Zero or near-zero minima of the generalized oscillator strength occur frequently, and their positions are related to the nodes of the radial wave functions for the states involved. Some general implications of the minima are discussed, and, as an example, experimental and theoretical results for a transition in Xe are presented.

The generalized oscillator strengths of atoms are currently being studied in substantial detail by refined experiments on the inelastic scattering of electron beams. Details of this important atomic property are not only related to the dynamics of the atomic electrons but also have implications for such phenomena as the passage of charged particles through matter. In this Letter we describe an aspect of the generalized oscillator strength, hitherto unnoticed, which appears to be a worthwhile target for future systematic studies.

The generalized oscillator strength $f_n(K)$ is an essential factor in the differential (first) Born cross section $d\sigma_n$ for the inelastic scattering of particles of charge Ze and velocity v by atoms and molecules:[1]

$$d\sigma_n=\frac{8\pi a_0^2Z^2}{mv^2/R}\frac{f_n(K)}{E_n/R}d\ln(Ka_0)^2, \tag{1}$$

where a_0 is the Bohr radius, m the electron mass, E_n the excitation energy, R the Rydberg energy, and $\vec{K}\hbar$ the momentum transfer. The generalized oscillator strength is defined as

$$f_n(K)=(E_n/R)(Ka_0)^{-2}|\epsilon_n(K)|^2, \tag{2}$$

in which the matrix element

$$\epsilon_n(K)=(n|\textstyle\sum_j\exp(i\vec{K}\cdot\vec{r}_j)|0) \tag{3}$$

is taken between the initial state 0 and the final state n, $\vec{r}_j$ being the position vector of the jth electron of the target. The sign of $\epsilon_n(K)$ depends both on the wave functions and on K. Whenever $\epsilon_n(K)$ changes sign as K varies, assuming the continuity of $\epsilon_n(K)$, $f_n(K)$ must go to a zero minimum.

Some instances of these minima were found earlier,[2-4] but apparently their implications and frequent occurrences were not noted. These minima and maxima are troughs and crests of the Bethe surface[5]—a three-dimensional plot of $f_n(K)$ as a function of E_n and $\ln(Ka_0)^2$. If a trough reaches the $K=0$ plane, the optical limit, it appears as a minimum, known as the Cooper mini-

mum,[6] in the photoabsorption cross section as function of the photon energy.

The occurrence of the first minimum of $f_n(K)$ for some discrete excitations of atoms can easily be understood from the Hartree-Fock (HF) or any independent-particle model by considerations similar to those that have been applied in the optical limit.[6] The HF orbitals are given in the form $r^{-1}P(r)Y_{lm}(\theta,\varphi)$ with Y_{lm} the appropriate spherical harmonic. For the ground and low-lying excited states of atoms the radial function $P(r)$ has the most prominent maximum beyond the outermost node. Let $P_n(r)$ and $P_0(r)$ be the radial functions of the active electron is states n and 0, respectively. Then the product $P_n(r)P_0(r)$ has the appearance of a cycle of a sine curve in the region between its most prominent minimum and maximum, and the center of the cycle coincides with the last node of the product. When the angular variables are integrated out, $\epsilon_n(K)$ becomes a linear combination of

$$\int_0^\infty P_n(r)j_\lambda(Kr)P_0(r)dr, \tag{4}$$

where $j_\lambda(Kr)$ is the spherical Bessel function of the first kind, and its order λ is limited by the orbital angular momenta l_0 and l_n, respectively, of the initial and final states.[7] For instance, for the $p^6 \rightarrow p^5 s$ transitions in the rare-gas atoms, only $\lambda = 1$ is allowed. If one chooses the value of K such that the first maximum of $j_1(Kr)$ (at $Kr \cong 2.1$) overlaps the last node of the product $P_n(r) \times P_0(r)$, then the integrand in $\epsilon_n(K)$ has roughly equal positive and negative areas. This argument can easily be generalized to other cases. The positions of the nodes of the HF orbitals are readily found from available tabulations.[8,9] The inclusion of electron correlation is not expected to change these results qualitatively. A systematic study should reveal cases where experimental detection of minima is particularly favorable. Indeed, the $f_n(K)$ for transitions between metastable and other excited states of He evaluated from correlated wave functions also show pronounced minima and maxima, although no minima [except for $(Ka_0)^2 = 0$ and ∞] were found in the transitions of He and H from the ground state.[10,11]

In reality, however, because of effects not included in the first Born approximation, the differential cross section may fail to vanish at the nodes of $\epsilon_n(K)$. In fact, the deviation of experimental cross sections in regard to the magnitudes and positions of the minima (or maxima) from those predicted by the procedure described above will serve as a test of the Born approximation as well as of the accuracy of the wave functions.[12]

The authors at the National Bureau of Standards have measured the electron-impact differential cross section for the excitation of Xe from the ground state to the $5p^5(^2P_{3/2}{}^\circ)6s$, $J = 1$, $E_n = 8.44$-eV state at an incident energy of 400 eV. The electron spectrometer, described elsewhere,[13] was used with an energy resolution of ± 0.25 eV. A check at higher energy resolution set the upper limits to the contribution from the nearby $J = 2$, $E_n = 8.32$-eV state at 5% and 10% for angles of 10 and 15°, respectively. An extrapolation to zero pressure was also made to avoid the contribution from double scattering—even at 5°—due to large elastic scattering cross section. The experimental cross sections at angles 3.75 to 15° in steps of 1.25° were measured relative to the 5° cross section, which was measured absolutely. The accuracy of the relative measurements for angles less than 10° is better than 5% and that of the absolute measurement is about 10%, including a correction for finite slit widths. The "experimental" $f_n(K)$ deduced from the experimental $d\sigma_n$ using Eq. (1) has a minimum at $(Ka_0)^2 \sim 0.7$ (Fig. 1).

The theoretical result in Fig. 1 was obtained from HF wave functions. In contrast to the work of Dow and Knox,[9] our excited-state wave func-

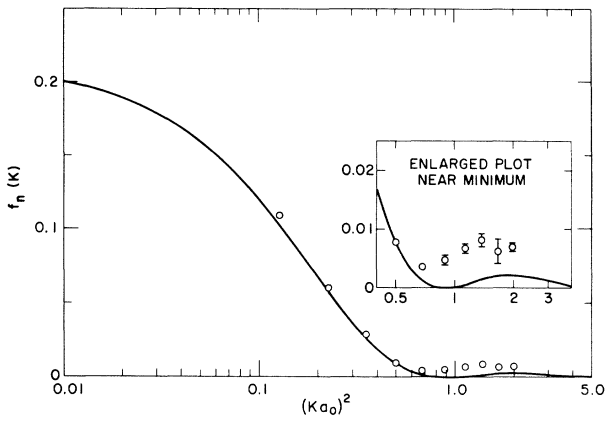

FIG. 1. The generalized oscillator strength $f_n(K)$ of Xe for the excitation to the $5p^5(^2P_{3/2}{}^\circ)6s$, $J = 1$, $E_n = 8.44$-eV state from the ground state. The solid line is the theoretical result calculated from the Hartree-Fock wave functions. The open circles are "experimental" values converted from the experimental differential cross section for the inelastic scattering of electrons by Xe at an incident energy of 400 eV. Error bars are 1 standard deviation of the data.

tion was calculated without freezing the core orbitals.[14] The allowance for spin-orbit coupling in the calculation was made in the same manner as in Ref. 9, with the excitation energy and spin-orbit coupling constants obtained from optical data.[15] Furthermore, we found that the inclusion of core orbitals hardly affected the $\epsilon_n(K)$ computed from $5p$ and $6s$ orbitals only, except for a reduction of its magnitude by less than 2%. According to our calculation, the optical limit $f_n(0)$ for the $E_n = 8.44$-eV ("triplet") transition is 0.212 and that for the $E_n = 9.57$-eV ("singlet") transition is 0.189, compared with the f values of 0.190 and 0.170, respectively, calculated by Dow and Knox.[9]

As can be seen from Fig. 1, the agreement between the HF result and the "experimental" $f_n(K)$ is good, though the "experimental" $f_n(K)$ does not vanish at the minimum. The experimental minimum occurs also at somewhat smaller $(Ka_0)^2$ than the calculated one and the subsequent maximum is larger than the HF result.

A preliminary experimental result on the $E_n = 10.03$-eV transition of Kr also shows a minimum of $f_n(K)$ at $(Ka_0)^2 \simeq 0.9$, compared with the theoretical minimum at $(Ka_0)^2 \simeq 1.20$. A minimum in the generalized oscillator strength of H_2O for the transition near $E_n = 7.4$ eV also have been studied.[2,16]

In conclusion, we hope that further experimental studies of this phenomenon will provide reliable data to test improved theoretical methods for collision problems as well as for atomic- and molecular-structure calculations.

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[2]For experimental data on H_2O, see E. N. Lassettre and E. R. White, The Ohio State University Research Foundation Scientific Report No. 12 (AFCRC-58-TN-406), 1958 (unpublished).

[3]For theoretical data on C_6H_6, see F. H. Read and G. L. Whiterod, Proc. Phys. Soc. (London) 85, 71 (1965); J. Karle, J. Chem. Phys. 35, 963 (1961).

[4]For theoretical data on Ar, see R. A. Bonham, J. Phys. Soc. Japan Suppl. 17, 10 (1962).

[5]M. Inokuti and R. L. Platzman, Abstracts of Papers, The Fourth International Conference on the Physics of Electronic and Atomic Collisions (Science Bookcrafters, Inc., New York, 1965), p. 408.

[6]J. W. Cooper, Phys. Rev. 128, 681 (1962); S. T. Manson and J. W. Cooper, Phys. Rev. 165, 126 (1968). For review articles, see U. Fano, Science 153, 522 (1966); U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 411 (1968).

[7]The allowed values of λ are $l_n + l_0, l_n + l_0 - 2, \cdots, |l_n - l_0| + 2$, and $|l_n - l_0|$.

[8]For the tabulation of the ground-state radial functions, see Charlotte Froese Fischer, "Some Hartree-Fock Results for the Atoms Helium to Radon," Department of Mathematics, University of British Columbia, January, 1968 (unpublished).

[9]For the tabulation of the excited-state radial functions of Kr and Xe, see J. D. Dow and R. S. Knox, Phys. Rev. 152, 50 (1966).

[10]For He, see Y.-K. Kim and M. Inokuti, Phys. Rev. (to be published), and references therein.

[11]For H, see M. Inokuti, Argonne National Laboratory Report No. ANL-7220, 1966 (unpublished), p. 1.

[12]Cross sections for the transitions to continua will in general not vanish at the minima because different types of transitions, that is, integrals (4) with different λ's, occur simultaneously at a given E_n.

[13]C. E. Kuyatt and J. A. Simpson, Rev. Sci. Instr. 38, 103 (1967).

[14]The theoretical $f_n(K)$ presented in Fig. 1 was calculated from the numerical HF wave functions computed with a program provided by Professor Charlotte Froese Fischer. See Ref. 8.

[15]C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular 467 (U.S. Government Printing Office, Washington, D.C., 1958), Vol. III.

[16]K. J. Miller, S. R. Mielczarek, and M. Krauss, to be published.