electrostatic field of symmetry \( C_{2v} \) was found to be small. There are no calculations for \( A_1(\text{III}) \) and \( B_1(\text{II}) \) using SCF-LCAO-MO virtual orbitals of the proper symmetry since none were obtained in the ground-state calculation.

The perturbation approach emphasizes the use of the best available core function and the best available excited orbital from the outset, without variation. Variation would allow the excited orbital to relax in the field of the molecular core but raises questions of orthogonality to the core. In this regard, the method of McWeeny and Öhrn\(^6\) is promising without requiring

\[ r \rightarrow \frac{C(6)}{r^5} \frac{a}{a + r} \]

Even if an excited orbital is obtained which is a variational solution in the field of the exact molecular core, two further effects remain to be evaluated. The "orbital average polarization" of the molecular core\(^7\) is the polarization of the core due to the smeared-out potential of the excited electron. This effect disappears in a complete SCF treatment of core plus electron. Secondly, the more important "core polarization" which arises from instantaneous polarization of the core by the excited electron is a correlation effect. Both of these effects are of spectroscopic importance.

\[^{6} R. \text{McWeeny}, \text{Tech. Rept. No. 59, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished); R. McWeeny and Y. Öhrn, } \text{iibid. No. 60; Rev. Mod. Phys.} \text{ 35, 520 (1963).} \]

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**Dipole–Quadrupole and Retardation Effects in Low-Energy Atom–Atom Scattering**

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Simple approximation formulas are derived for the dipole–quadrupole and retardation effects upon the total elastic scattering cross section for atomic collisions in the thermal energy range. For a long-range potential containing both the dipole–dipole and dipole–quadrupole terms, i.e., \( V(r) = -(C(6)/r^6)[1 + (\beta/r^2)] \), one finds \( \Delta Q/Q_{\text{MM}} \approx 3\beta(\partial Q_{\text{MM}}/\partial \beta) \) where \( Q_{\text{MM}} \) is the Massey–Mohr cross section for an inverse sixth-power attraction. For a long-range potential including dipole–dipole and retardation effects, approximated by \( V(r) = -(C(6)/r^6)[\alpha/(\alpha + r)] \), one obtains \( \Delta Q/Q_{\text{MM}} \approx -(\alpha^2 Q_{\text{MM}})/\alpha \). Since these deviations are small and opposite in sign, it is concluded that the contributions of the dipole–quadrupole and retardation effects to the total cross sections are not sufficient to account for any significant discrepancy between theoretical and experimental \( Q \) values.

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**I. INTRODUCTION**

The principal objective of low-energy atomic scattering experiments is the determination of the long-range part of the interaction potential, for comparison with theory. The data are usually interpreted on the assumption that the potential at large separations is of the London inverse sixth-power functional form. For the general case of a potential with asymptotic behavior \( V(r) = -C(6)/r^6 \), one expects the total elastic scattering cross section to be well approximated by the Massey–Mohr relationship \( Q(\nu) \propto (C(6)/\nu)^{6(1-\gamma)} \), where \( \nu \) is the relative velocity. In addition, the low-angle "classical" differential cross section should be given by \( I(\theta) \propto \theta^{-2(1+s)} \). There is a considerable body of evidence\(^8\) from both total and differential cross sections that \( s \) is very close to the expected value of 6. In addition, relative values of \( Q \)'s are found to correlate well\(^9\) with theoretical estimates of \( C \) for a large number of atomic (and molecular) systems. Unfortunately, absolute values of \( C \) derived from experimental \( Q \)'s appear\(^9\) to be somewhat larger than predicted values based on perturbation theory calculations. This discrepancy may well be due to a common systematic experimental error; alternately, it could be an indication that the long-range attraction is somewhat stronger than that


\[^{9} E. \text{W. Rothe and R. B. Bernstein, J. Chem. Phys.} \text{ 31, 1619 (1959).} \]

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**References**

\[^{6} \text{O. Sinanoglu, J. Chem. Phys.} \text{ 33, 1212 (1960).} \]

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\[^{7} \text{R. McWeeny, Tech. Rept. No. 59, Quantum Chemistry Group, Uppsala University, Uppsala, Sweden (unpublished); R. McWeeny and Y. Öhrn, iibid. No. 60; Rev. Mod. Phys.} \text{ 35, 520 (1963).} \]

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\[^{9} \text{E. W. Rothe and R. B. Bernstein, J. Chem. Phys.} \text{ 31, 1619 (1959).} \]

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\[^{1} \text{H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. (London)} \text{ A144, 188 (1934).} \]

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\[^{2} \text{H. Pauly, Fortsch. Physik 9, 613 (1961).} \]

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\[^{3} \text{A. Dalgarno, Rev. Mod. Phys.} \text{ 35, 611 (1963); also Refs. 2-4.} \]
predicted by perturbation theory considering only the induced-dipole interaction. In the present paper we examine the influence of the usually neglected terms in the potential such as the dipole–quadrupole interaction \( r^{-8} \) and the retardation effect \( r^{-7} \) at large separations.

The approach used is a direct extension of the Massey–Mohr \(^1\) (MM) semiclassical approximation technique. The results are expressed in terms of the fractional deviation \( (Q - Q_{MM})/Q_{MM} \), where \( Q_{MM} = 7.547(C/\hbar v) \). Although it has been shown \(^6\) that the Schiff–Landau–Lifshitz (SLL) approximation formula for \( Q \) (the same as that of MM with a 7.5% greater numerical factor) is more exact, the MM procedure is better adapted to the present problem and has therefore been chosen. In any case, the fractional effect \( \Delta Q/Q \) should be very nearly correct. The present results should be applicable over the same range of velocities as the MM or SLL approximations. They all lose validity at low \( v \) due to the failure of the semiclassical assumptions and at high \( v \) due to the increasing importance of the short-range repulsion.

II. DIPOLE–QUADRUPOLE EFFECT

Including the \( r^{-8} \) dipole–quadrupole contribution the long-range interatomic potential becomes

\[
V(r) = -(C^{(6)}/r^8)[1 + (\beta/r^2)],
\]

where \( \beta = C^{(6)}/C^{(0)} \) with \( C^{(6)} \) denoting the dipole–quadrupole constant and \( C^{(0)} \) the dipole–dipole constant.

If one uses the London approach to calculate the interatomic potential then \( C^{(6)} \) as well as \( C^{(0)} \) can be given in closed form. In the equations that follow, the subscripts on the \( f \) values (oscillator strengths), polarizabilities \( \alpha \), and ionization energies \( E \) refer to the two interacting atoms. The results are expressed in atomic units:

\[
C^{(0)} = \frac{\hbar}{\pi} \left[ \alpha_1 \alpha_2 E_1 E_2 / (E_1 + E_2) \right],
\]

\[
C^{(6)} = \frac{45}{8} \left[ \alpha_1 \alpha_2 E_1 E_2 / (E_1 + E_2)^2 + \alpha_1^2 \alpha_2 E_1^2 E_2 \right].
\]

The total collision cross section is then calculated by assuming the usual semiclassical conditions \(^1\) \( ^2 \) \( ^8 \)

\[
Q = Q_+ + Q_\to = \frac{2\pi L^2}{\hbar^2} \int \frac{8\pi \tau^r}{kL} \eta_B \eta_{BB}^r d\Omega,
\]

where \( \eta_B = \eta_B^{(6)}[1 + \pi(\beta k^2 P^2)] \),

\[
\eta_B^{(6)} = \frac{3\hbar \pi (\mu C^{(6)} k^4 / \hbar^2 P^2)},
\]

and \( L \) is defined by the equation

\[
\eta_B(L) = \frac{1}{2} x^2 (1 + \varphi x^2),
\]

where \( x = L_0/L \). Here,

\[
\varphi = \frac{3}{8} \beta \left[ 3 \pi C^{(0)}/8 \hbar v \right] - 1 = \frac{1}{2} \pi (\beta/Q_{MM}),
\]

and

\[
Q_{MM} = \frac{3\pi}{8} \pi \left( \frac{L_0}{k} \right)^2 = \frac{3\pi}{8} \left( \frac{C^{(6)}/8 \hbar v} \right) \frac{L_0}{k}.
\]

Evaluation of (4) yields

\[
Q = 2\pi \left( L_0/k \right)^2 \left[ 1 + \frac{3}{3} \varphi \left[ 1 + \frac{3}{3} \varphi x^2 + \frac{3}{3} \varphi x^4 \right] \right] \frac{1}{1 - \varphi}.
\]

For most cases of practical interest, \( \varphi \ll 1 \) and \( x \approx 1 - \varphi/5 \). Under these conditions, one obtains the following approximate result valid to first order in \( \varphi \) for the fractional deviation

\[
\Delta Q/Q_{MM} \approx \frac{2\pi}{3} \varphi = 2\pi \beta / 3Q_{MM}.
\]

In Fig. 1 we have plotted \( \Delta Q/Q_{MM} \) [using Eq. (13)] vs the relative velocity \( v \) for two systems where total cross sections have been measured experimentally. \(^9\) It is seen that for the thermal-energy region, say from \( 10^4 \) to \( 10^5 \) cm/sec, the deviation is only a few percent. For the curves labeled K–M we used a value for \( C^{(6)} \) obtained from the variational calculations of Kirkwood and Müller. \(^10\) Since the London results for the interatomic potential provide a lower limit and the Kirkwood–Müller calculations an effective upper limit, a more precise determination of \( C^{(6)} \) and \( C^{(0)} \) would yield a result for \( \Delta Q/Q_{MM} \) that lies somewhere within the shaded area. The curves for Ne–Ar, Ar–Ar, and Kr–Ar fit smoothly between the curves for the He–Ar and Xe–Ar interactions. The results for \( v > 10^5 \) cm/sec should be considered with caution since for such high velocities the repulsive forces become very important (see Ref. 8) and the form of \( V \) in Eq. (1) is no longer a good approximation.

III. RETARDATION EFFECT

The retardation effect arises from the interaction of the electrons with the radiation field and at large interatomic separations the effect modifies the dipole–dipole

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van der Waals force. The interaction becomes more attractive and for \( r \to \infty \) the modified potential has a \( r^{-3} \) dependence. One might thus expect that the retardation increases the total collision cross section. The interaction constant, however, changes too, and depending on the magnitude of the relative velocity, the cross section can change in either direction.

The effect of the retardation is to multiply the dipole–dipole potential by a function which goes as \( r^{-1} \) at large interatomic separations and becomes unity at small distances. Casimir and Polder have calculated this function for atoms with closed-shell configurations.\(^{11}\) There results are given in numerical form; for our purpose it was necessary to find an empirical function to describe the retardation effect. The parameter in this function which determines at what separations the \( r^{-1} \) dependence takes over is related to the longest wavelength of the dipole transitions in the separate atoms. If we define a reduced distance \( r' = r/\lambda \), where \( \lambda \) is the wavelength mentioned above, then one possible empirical function is given by

\[
f(r') = \frac{a/\lambda}{r'+a/\lambda}, \tag{14}\]

This function has the proper behavior at large as well as at small interatomic distances and it also agrees well with the Casimir–Polder calculations. The constant \( a \) must be adjusted to give the proper fit. The useful range of \( a/\lambda \) is from 0.54 to 0.75. The modified interaction potential now becomes

\[
V(r) = - \frac{(C(0)/r^6)f(r)}{r'}, \tag{15}\]

where

\[
f(r') = \frac{a}{r'+a/\lambda}. \tag{16}\]

With this potential we can now calculate the JB phase shift and then the cross section. Thus

\[
\eta_{J\beta} = \eta_{J\beta}^{(0)} \left[ 1 - \frac{32}{9\pi} \rho + \frac{4}{3\pi} \rho^3 + \frac{8}{3\pi} \rho^5 - \frac{16}{3\pi} f(\rho) \right], \tag{18}\]

where \( \eta_{J\beta}^{(0)} \) has been defined in Eq. (6), \( \rho = b/a = (L_0/ka)(l/L_0) \), and

\[
J(\rho) = \begin{cases} \frac{(1-\rho^2)^{-1}}{2(\rho^2-1)^{-1}} \tan^{-1}[(\rho-1)/(\rho+1)], \quad \rho > 1 \\ 1, \quad \rho = 1 \\ 2(\rho^2-1)^{-1} \tan^{-1}[(\rho-1)/(\rho+1)], \quad \rho < 1 \end{cases} \tag{19}\]

For small \( \rho \) the phase shift can be approximated by

\[
\eta_{J\beta} = \eta_{J\beta}^{(0)} \left[ 1 - (32/9\pi) \rho \right], \tag{20}\]

\(^{11}\) A. B. G. Casimir and D. Polder, Phys. Rev. 73, 360 (1948).
while for $\rho \to \infty$ expansion of $J(\rho)$ in inverse powers of $\rho$ exactly cancels all the terms in the bracket of Eq. (18), and the remaining terms in the expansion yield the asymptotic result.

$$\eta_{MB} = 17J_{B}^{(6)}[(128/45\pi)\rho^{1} - 3/6\rho^{2} + \cdots]$$
$$= 17J_{B}^{(6)}[1 - 3/5\alpha \pi (a/b) + \cdots]$$
$$= 17J_{B}^{(7)}[1 - 3/5\alpha \pi (a/b) + \cdots], \quad (21)$$

where $\eta_{MB}^{(7)}$ is the phase shift of the potential

$$V(r) = -(C^{(6)}a/r^{7}) = -(C^{(7)}/r^{7}). \quad (22)$$

Thus, for very large impact parameters ($\rho \to \infty$), Eq. (21) yields the expected phase shift.

In most scattering experiments the characteristic values of the impact parameters are considerably smaller than the constant $a$ of Eq. (16), and thus to a good approximation the total collision cross section can be calculated by using Eq. (20) for the phase shift. The contributions of the phase shift for $\rho > 1$ to the collision cross section are negligible for the velocity range considered.

To determine the lower limit of the integral in Eq. (4) we again consider

$$\eta_{MB}(L) = \frac{1}{2} = \frac{1}{2}a^{6}[1 - (\psi/x)], \quad (23)$$

where $x = L_{0}/L$, and

$$\psi = (32/9\pi)(L_{0}/ka). \quad (24)$$

Since $\psi \ll 1$,

$$x \approx 1 + (\psi/5). \quad (25)$$

Substitution of (20) and (25) into (4) and evaluation of the integral yields

$$Q = (2\pi L_{0}^{2}/\hbar^{2}a^{2})[1 + \frac{1}{8}[1 - \frac{1}{16}(\psi/x) + \cdots]]; \quad (26)$$

and thus the fractional deviation from the dipole–dipole (MM) cross section becomes

$$\frac{\Delta Q}{Q_{MM}} = 8704 \frac{Q_{MM}}{8505\pi^{3}a}. \quad (28)$$

In Fig. 2 we have plotted $\Delta Q/Q_{MM}$ of (28) for He–Ar and Xe–Ar. Again a more sophisticated calculation of the interaction constant $C^{(6)}$ would yield a result somewhere within the shaded area. As seen from Eq. (28), the retardation effect lowers the total cross section. This indicates that the change of the interaction constant is more important than the effect of the more attractive potential ($r^{-6}$).

**IV. COMBINED EFFECTS**

In Fig. 3 we have plotted the fractional deviation from the dipole–dipole cross section due to the combined dipole–quadrupole and retardation effects. [The effects of the retardation on the dipole–quadrupole interaction is, of course, not included. The change of $Q$, however, should be very small since $f(r)$ is very close to one in the region where the dipole–quadrupole interaction makes a significant contribution.] It is interesting to note that in the velocity range of experimental interest the two effects almost cancel each other.

These results clearly show that neither the dipole–quadrupole nor the retardation effects make a large enough contribution to explain any discrepancies (Sec. I) between theory and experiment. It appears that in the framework of the perturbation approach the dipole–dipole interaction provides by far the largest contribution to the collision cross section. It is true, however, that a very small change in the power of the $r^{-6}$ interaction can change the resulting cross section significantly, and it may be that a variational calculation of the atom–atom interaction energy would yield a power dependence ($s$) that is slightly different from the value 6.0.