Stark Broadening of Isolated Lines of Neutral Atoms

by

J. Cooper
Joint Institute for Laboratory Astrophysics

and

G. K. Oertel
National Aeronautics and Space Administration
Washington, D. C.

NOTICE
This research was supported in part by the Advanced Research Projects Agency of the Department of Defense, monitored by Army Research Office-Durham under Contract No. DA-31-124-ARO-D-139, and in part by the Directorate, Goddard Space Flight Center, National Aeronautics and Space Administration.

A briefer paper on this work will appear in The Physical Review. This report includes additional Appendices and tabular material not heretofore published.

University of Colorado
Boulder, Colorado
June 15, 1969
I. INTRODUCTION

The modern theory of Stark broadening of isolated spectral lines is based upon the comprehensive paper by Griem, Baranger, Kolb and Oertel\(^1\) (GBKO). They give explicit expressions for the width and shift in terms of the S-matrix elements for an electron collision, and the same expressions are obtained by Cooper\(^2\) using a density matrix formulation of the impact approximation. The GBKO theory has proved highly successful in predicting widths and shifts of isolated lines of neutrals, especially helium.\(^3,4\) However, experiments (first independently by Jalufka et al.\(^5\) and by Popenoe and Shumaker\(^6\)) have shown that for ion lines the GBKO widths are often too small (by factors of 2 to 10). This has led to a number of theoretical papers (e.g., by Griem,\(^7,8\) Brechot,\(^9\) and Davis and Roberts\(^10\)) on ion broadening. We first tested a suggestion by Baranger\(^11\) and found good agreement with experiments.\(^12\) In further pursuit of the subject we are applying the methods of GBKO to ions, notably by using hyperbolic rather than straight classical paths. This confirms that strong (elastic) collisions contribute heavily (∼50%) to the width,\(^7\) but in most cases leaves our numerical results\(^12\) unchanged within a few percent. In the course of that investigation, to be published later, we made certain additions and corrections to the GBKO theory which affect neutral broadening as well. Some of these are numerically significant only when the level spacing is comparable with the thermal energy. This is the case for some neutrals as well as ions, but not for helium. New results for helium are presented nevertheless, because of its importance in plasma diagnostics and because of the existence of accurate measurements (e.g., Berg et al.,\(^13\) Lincke,\(^14\) Greig et al.\(^15\)).

We have not made changes in the GBKO approach to broadening by ions except for a generalization of the equation for the quasistatic broadening parameter, \(\alpha\) (see Eq. (29)). Consequently, this report deals entirely with
electron impact broadening, and the inclusion of ion effects still should
be carried out according to GBKO.

Seaton has shown that quantum effects in excitation of neutral atoms
by electron impact can be described significantly better by a classical path
theory if all expressions which contain the perturber (electron) velocity are
symmetrized with respect to initial and final velocities. Symmetrization is
not necessary when the width is expressed in terms of the forward scattering
amplitude \( f(0) \) for the perturbers, because one stays on the energy shell.
However, when the optical theorem is used to express \( f(0) \) in terms of elastic
and inelastic scattering amplitudes and cross sections it becomes reasonable
to use symmetrization for the latter, but not the former. In this sense, we
have carried out symmetrization in the present version of the GBKO theory.
It may be considered as an approximate way to account for "back reaction" of
atom on perturber and is most important near threshold, or at low temperatures.

Two approximations in the GBKO theory are the Dyson expansion of the
Schroedinger equation for the time development operator (or the S-matrix) and
the multipole expansion. Only the first nontrivial terms in each of the two
expansions are used in GBKO, but while there is a correction for higher
order terms in the Dyson series (in the form of the strong collision term)
there is no similar correction for higher multipoles. It was therefore under-
taken to work out the next higher order multipole, i.e., the quadrupole term.
It was not expected to find more than a correction; however, it turns out that
there are circumstances in which the multipole series is rapidly convergent,
but in which nevertheless the quadrupole contribution exceeds that of the
dipole in the second order (weak collision) term. The range of conditions
under which this will happen is delineated and it is shown that normally the
quadrupole contribution remains small. It sometimes gets large at very low
temperatures when the dipole threshold greatly exceeds the quadrupole threshold for inelastic collisions. In the latter case, one expects that higher order Dyson terms (elastic collisions) likewise become important and this is indeed reflected in a dominance of the strong collision term when such cases are considered. However, when the strong collision term is large the accuracy of the results will be questionable.

A new look at the complex function arising from the first nontrivial term in the Dyson expansion led to an analytic form for the real part $a(z)$, and the discovery of an apparent error in the numerical computation which led to $a(z)$ and $b(z)$ in GBKO. The resulting reduction in the width is only about 2% for typical He I lines, but approaches 10% in some cases where the level spacing is large compared with the inverse collision time. A general form for the coefficients of the asymptotic expansion for $z^{\infty}$ of the imaginary parts $B(z)$ and $b(z)$ was found and led to a significant reduction of the GBKO values for $b(z)$ at $z \leq 3$, (with a consequent reduction of typically 10% in the magnitude of the shift).

The present numerical results take lower level broadening into account. While this is true also for the GBKO results, it is not so for other numerical results based on the GBKO paper. Again, this is usually more important in lines of heavier neutrals.

Debye shielding becomes important when the plasma frequency approaches the level spacing. It leads to a saturation-like reduction in the normally linear increase of impact width and shift with electron density. While the equivalent cutoff in the integration over impact parameters in GBKO was worked out for the high velocity limit, numerical work shows that most of the shielding takes place at low velocities where an equivalent cutoff cannot be readily obtained with the GBKO approach. Nevertheless, Debye shielding is included
in this fashion in the present treatment, and numerical results are presented for the He I 5016 line for which experimental data are available.\textsuperscript{15}

It was recently proposed by Chappell et al.\textsuperscript{19} that in the low velocity limit both electric fields in the correlation function should be shielded rather than just one as in GBKO. While this may overestimate the shielding effects it would seem that it should provide an upper limit for them. The functions $A$ and $a$ can be obtained in simple analytic forms and reduce to the unshielded functions in the low density limit. Details of this treatment, which eliminates the need for a cutoff at large impact parameters, as well as a comparison with experimental results,\textsuperscript{15} will be the subject of a subsequent paper.

The reported contributions constitute additions and improvements of the GBKO theory rather than a different approach. They should definitely improve the theory consistent with its foundation, although numerical results do not change by very much in helium.

Section II deals with the theoretical developments and provides formulae for practical computations. Some validity criteria are also discussed. Results and discussion are presented in Section III. Appendix A gives details on the functions $A$, $a$, $B$ and $b$ of GBKO. Alternate derivations of angular averaging constitute Appendices B and C and details of the symmetrization are in Appendix D.

II. THEORETICAL DEVELOPMENTS

The derivation of a useful relation for Stark broadening by electron impacts starts from a Fourier analysis of the equation for power radiated in a general quantum mechanical system in a transition from state $|i\rangle$ to state $|f\rangle$.\textsuperscript{4,11} It is necessary to invoke the impact approximation (or some other restricting approximation). Validity criteria were discussed in some detail by Baranger.\textsuperscript{11}
The electron impact width $w$ and shift $d$ of an isolated line with upper state $|i\rangle$ and lower state $|f\rangle$ can be obtained from

$$w + id = N_e \int_0^\infty \rho_{\text{max}} \int_0^\rho v f(v) \, dv \, 2\pi \rho d\rho \left\{1 - \langle i | S | i \rangle < f | S^{-1} | f \rangle \right\}_{\text{Av}}$$

in terms of the $S$-matrix for a collision of a single electron with the atom. Notice, we need only a diagonal term for an isolated line. The curly brackets $\{\}_{\text{Av}}$ indicate an angular average, the thermal average is completed by the integration over velocities $v$. To allow for correlation effects between the electrons, GBKO indicate that the cutoff in the integration over impact parameters $\rho$ should come at $\rho_{\text{max}} = 1.123 \rho_D$, the Debye radius. This will reduce the otherwise linear increase with the electron density $N_e$.

It is customary to use a perturbation expansion for the $S$-matrix elements (the Dyson expansion), which can be written as

$$S = 1 - \frac{1}{i\hbar} \int_{-\infty}^\infty dt \, \tilde{V}(t) + \frac{1}{(i\hbar)^2} \int_{-\infty}^\infty dt_1 \, \tilde{V}(t_1) \int_{-\infty}^{t_1} dt_2 \, \tilde{V}(t_2) + \ldots$$

in terms of the potential operator $\tilde{V}(t)$ in the interaction representation:

$$\tilde{V}(t) = e^{iH_0 t / \hbar} \, V(t) \, e^{-iH_0 t / \hbar}$$

$V(t)$ is the time dependent interaction of the perturbing electrons with the atom during the collision, and $H_0$ is the unperturbed Hamiltonian (i.e., $H_0 |j\rangle = E_j |j\rangle$). Usually only the first nonvanishing order (the second) of the Dyson series is taken. The first order term averages out to zero due to symmetry (See Appendices B and C).
To second order in the Dyson expansion results\(^1\)

\[
(1 - \langle i | S | i \rangle \langle f | S^{-1} | f \rangle)_{\text{Av}} = \frac{1}{\hbar^2} \{ \langle F_{ii} \rangle + \langle F_{ff} \rangle - \langle F_{if} \rangle \}, \tag{4}
\]

with

\[
\langle F_{jj} \rangle \equiv \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{1} dt_2 \overline{V}_j(t_1) \overline{V}_j(t_2), \quad j = i, f \tag{5}
\]

and

\[
\langle F_{if} \rangle = -\int_{-\infty}^{\infty} \overline{V}_i(t) dt \int_{-\infty}^{\infty} \overline{V}_f(t) dt, \text{ where } \overline{V}_j(t) = \langle j | \overline{V}(t) | j \rangle, \text{ etc. }.
\]

This second order term diverges at small impact parameters, which is obviously unphysical since we know that the unitarity condition restricts the S-matrix elements to be less than unity. In fact, we can write the elements as follows\(^1\)

\[
\langle i | S | i \rangle = e^{-\eta_i - i\phi_i},
\]

where \(\phi_i\) is a real phase shift (due to elastic collisions) and \(\eta_i\) is a real positive number (associated with inelastic collisions). The perturbation expansion is essentially equivalent to

\[
\langle i | S | i \rangle = e^{-\eta_i - i\phi_i} = 1 - \eta_i - i\phi_i + \ldots, \tag{6}
\]

which obviously breaks down when \(|\eta_i + i\phi_i| \sim 1\). The so-called "strong-collision cutoff" in the \(\rho\) integration is then obtained as that impact parameter \(\rho_{\text{min}}\) for which\(^1\) (using Eq. (4)).

\[
|1 - \langle i | S | i \rangle \langle f | S^{-1} | f \rangle| = 1 \tag{7}
\]
For impact parameters less than this \( \rho_{\text{min}} \) it is assumed that the phase-shifts and inelastic effects due to interaction of the electron with the atom are so large that the S-matrix elements either oscillate rapidly (bounded by +1 and -1) or approach zero. Then \( \{1 - i|S|i\rangle \langle f|S^{-1}|f\rangle\}_{\text{Av}} \) can be replaced approximately by its mean value of unity for \( \rho < \rho_{\text{min}} \). This gives

\[
\mathbf{w} + \mathbf{d} = N_e \int_0^\infty f(v)vdv \int_0^{\rho_{\text{max}}} 2\pi \rho d\rho \{1 - i|S|i\rangle \langle f|S^{-1}|f\rangle\}_{\text{Av}}
\]

\[
+ N_e \int_0^\infty f(v)vdv \pi \rho_{\text{min}}^2
\]

This second term is often referred to as the Lorentz-Weisskopf term.\(^4\)

Other equivalent strong-collision cutoffs can be used,\(^1\) but if the theory is to be accurate the results should be insensitive to the choice (i.e., one ought to be able to replace the 1 on the right hand side of Eq. (7) by 0.8 or 1.2).

The potential \( V(t) \) is computed in the classical path approximation\(^1,4,11\) (perturbing electron traveling on a straight line path with speed \( v \) and impact parameter \( \rho \)). The potential is then

\[
V(t) = \frac{e^2}{|\mathbf{r}|^2} \left( \frac{\mathbf{R} \cdot \mathbf{r}}{|\mathbf{r}|^2} + \frac{3(\mathbf{R} \cdot \mathbf{r})^2 - \mathbf{r}^2 \mathbf{R}^2}{2|\mathbf{r}|^4} \right),
\]

to second order in the expansion parameter \( \frac{|\mathbf{R}|}{|\mathbf{r}|} \), (i.e., including the quadrupole term), in terms of the atomic coordinate vector \( \mathbf{R} \) and the perturber-nucleus distance \( \mathbf{r} = \rho + v \mathbf{t} \). Only the first term in the brackets is treated in GBKO.

It is possible to proceed from here in two equivalent ways. The angular average may be carried out over perturber paths with the atom orientation held fixed,\(^1\) or the perturber path may be held fixed and the average carried
out over orientations of the atom. The latter approach is equivalent to a summation over magnetic quantum numbers and results in a more convenient expression for the interference term; the former is more transparent from a physical point of view. After some algebra we obtain

\[
\langle F_{jj} \rangle_{\text{AV}} = \kappa^2 \left( \frac{\lambda}{\rho} \right)^2 \left[ \frac{2}{3} \sum_{j'} R_{jj'}^2 \left( A_2(|z_{jj'}\rangle) + i B_2(z_{jj'}\rangle) \right) + \frac{1}{10} \left( \frac{a_0}{\rho} \right)^2 \sum_{j''} R_{jj''}^4 \left( A_4(|z_{jj''}\rangle) + i B_4(z_{jj''}\rangle) \right) \right]
\]

\[ (j=i,f) \tag{10} \]

(the B terms are negative for \( j = f \)), and

\[
\langle \langle F_{if} \rangle \rangle_{\text{AV}} = \kappa^2 \left( \frac{\lambda}{\rho} \right)^2 \cdot \frac{4}{15} \frac{a_0^2}{\rho^2} \left( -1 \right)^{J_i+J_f-1} \left\{ \begin{array}{cc} J_i & 2 \\ J_f & 1 \end{array} \right\} R_{ii}^2 R_{ff}^2, \tag{11} \]

where \( \kappa = \hbar/mv \) is the de Broglie length divided by \( 2\pi \). The matrix elements are, in units of the Bohr radius \( a_o \),

\[
R_{jj'}^2 \equiv \frac{1}{2J_j+1} \sum_{m} \sum_{m'} |<j|R|m'>|^2 = \frac{1}{2J_j+1} (J_j||\hat{R}C(1)||J_j')^2 \tag{12} \]

and

\[
R_{jj}^2 = \langle J_j||\hat{R}^2C(2)||J_j \rangle \]

and

\[
R_{jj'}^4 \equiv \frac{1}{2J_j+1} \sum_{m} \sum_{m'} |<j|R^2|m'>|^2 = \frac{1}{2J_j+1} (J_j||\hat{R}^2C(2)||J_j')^2. \tag{13} \]

The expressions to the right of the equalities are reduced matrix elements (see appendices B and C). \( J_j \) is the total angular momentum quantum number of state \(|j\rangle\) of the atom. The double integration in the Dyson term in Eq. (5)
is now contained in the functions A and B, which are discussed in Appendix A. Alternate derivations for Eq. (10) and also a derivation for Eq. (11) are given in Appendices B and C. The 6-j symbol is such that the interference term remains negative. As in GBKO the parameter \( z_{jj'} = \frac{\omega_{jj'}}{\omega} \) is used as the argument of functions A and B, but now the second term in Eq. (10) (i.e., the quadrupole term) as well as the quadrupole interference term (Eq. (11)) are included (\( \Delta E_{jj'} = E_j - E_{j'} \)). Seaton, Stauffer and McDowell and Tsao and Curnette have found the functions \( A_2, a_2 \) and \( A_4 \), respectively, independently in connection with dipole and quadrupole electron-impact excitation cross sections.

The intimate relation between electron broadening and electron-atom collisions is again evident in the present frame work, i.e., the inelastic contribution can be expressed directly in terms of inelastic collision cross sections. This can easily be seen, for, ignoring the interference term (elastic), the real part of \( \{ 1 - i |S| i' < f | S^{-1} | f' \} A_v \), (proportional to the \( A' s \)) can be written

\[
\text{Re}(1 - i |S| i' < f | S^{-1} | f') A_v = \frac{1}{\hbar^2} \sum_{i'f} \int_{-\infty}^{\infty} dt_1 e^{i \omega_{ii'} t_1} <i' | V(t) | i'> \int_{-\infty}^{t_1} dt_2 e^{-i \omega_{ii'} t_2} dt_2 + \text{equivalent term with } i \rightarrow f \text{ and } i' \rightarrow f'
\]

\[
= \frac{1}{2} (\Sigma_i P_{ii'} + \Sigma_{f'} P_{ff'})
\]

(14)

if we identify the transition probability for a transition from state

\[
|i\rangle \rightarrow |i'\rangle \text{ with } P_{ii'} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} e^{i \omega_{ii'} t} dt^2 \]

(15)

Integration over impact parameters then gives the width in terms of the velocity integral over the inelastic cross sections, since \( \sigma_{ij} = \int_0^{\infty} 2\pi \rho_1 P_{ij} (\rho_1) d\rho_1 \).
In the classical path approximation the path of the perturbing electron is supposed to be independent of the state of the atom. However, for the inelastic transition from $|i\rangle$ to $|j\rangle$, separated by $\Delta E_{ij}$, there is a change in velocity such that $\frac{m}{2}(v_i^2 - v_f^2) = \Delta E_{ij}$. Seaton and Alder et al. find that with a suitable average between initial and final states (symmetrization), the classical path calculations for the cross sections can give much better agreement with the full quantum-mechanical calculations than unsymmetrized calculations. This symmetrization of the present parameter $z$ (Seaton's $\beta$) is found to give reasonably good results even near threshold, where the tacit assumption $v_i \gg v_f$ is violated. In following this procedure the "back-reaction" of atom on perturber is taken into account to some extent.

As discussed in Appendix D, we use Seaton's symmetrization for the $A$ functions, namely

$$z_{jj'} = z_{jj'} \frac{\rho v_o |j\rangle}{v^2 (\gamma_{jj'}^o / m)}.$$  \hspace{1cm} (16)

Also we put $A=0$ if $v^2 < 2\kappa_{jj'} / m$ (i.e., velocity integration started at threshold). Factors such as $(\rho v_o^2)$ multiplying the $A_4$ function are also symmetrized, (Appendix D) but the $B$ functions (which correspond to elastic terms) are NOT symmetrized, so that the adiabatic limit is obtained, i.e., we use

$$z_{jj'} = \rho \frac{\omega |j\rangle}{v} \text{ in the } B \text{ functions.} \hspace{1cm} (17)$$

The minimum impact parameter $\rho_{\text{min}}$ can now be obtained from Eqs. (7), (4), (10) and (11). In the resulting equation all $A$'s are zero below threshold. With the upper limit $\rho_{\text{max}}$ the integration in Eq. (1) can now be carried out. It is convenient to integrate over the unsymmetrized version, and carry out the symmetrization on the resulting expression. This yields, similarly,
\[ w + id = N \int_0^\infty f(v)vdv \left( \hat{\rho}_{\text{min}}^2 + \frac{4\pi}{3} \chi^2 \sum_i R_{ii}^2, \{ a_2 | \hat{z}_{\text{min}} | \} \right) \]

\[ - a_2 \left( | \hat{z}_{\text{max}} | \right) + i b_2 \left( | \hat{z}_{\text{min}}^i | \right) - 1b_2 \left( | \hat{z}_{\text{max}}^i | \right) \]

\[ + \frac{\pi a_2}{5} \sum_{i} \left( \frac{\omega_{ii}^2}{\omega_{ii}^2 + \omega_{ii}^2} \right) R_{ii}^2 \left( \frac{a_4 (| \hat{z}_{\text{min}}^i |) - a_4 (| \hat{z}_{\text{max}}^i |)}{v^2 - \omega_{ii}^2} + \frac{1}{2} b_4 \left( | \hat{z}_{\text{min}}^i | \right) - \frac{1}{2} b_4 \left( | \hat{z}_{\text{max}}^i | \right) \right) \]

+ equivalent terms with \( i \rightarrow f \) (with the sign of the \( b \) functions altered)

\[ - \frac{4\pi}{15} \sum_i \left( \frac{\omega_{ii}^2}{\omega_{ii}^2 + \omega_{ii}^2} \right) R_{ii}^2 \left( \frac{1}{2} b_4 \left( | \hat{z}_{\text{min}}^i | \right) - \frac{1}{2} b_4 \left( | \hat{z}_{\text{max}}^i | \right) \right), \quad (18) \]

with \( \hat{\rho}_{\text{min}} = \text{Min} (\rho_{\text{min}}^i, \rho_{\text{max}}^i) \). The first term in the square brackets is the strong collision term. \(^1\) It represents an estimate of the higher order terms in the Dyson expansion as indicated earlier. The functions \( a \) and \( b \) (subscripts: 2 for dipole, 4 for quadrupole) are defined and discussed in Appendix A. The remaining integration is usually started at \( v = 0 \) with the provision that \( a_2 \) and \( a_4 \) are zero below threshold for excitation \( (\omega_{jj}^i > 0) \). A check on the validity of the classical path approximation and the symmetrization procedure is provided by a low velocity cutoff at \( \chi = \rho_{\text{min}} \), or \( v = \chi / m \rho_{\text{min}} \), since impacts with \( \rho < \chi \) would certainly require a quantum mechanical (rather than classical path) treatment. Thus, in determining \( z \) and \( \hat{z} \), and inserting in Eq. (18), \( \rho_{\text{min}} \) is now replaced by

\[ \hat{\rho}_{\text{min}} = \text{Max} (\rho_{\text{min}}^i, \chi), \quad (19) \]

and the strong collision term takes the form

\[ \pi \left( \frac{\hat{\rho}_{\text{min}}^2}{\hat{\rho}_{\text{min}}^2 - \chi^2} \right) \text{ for } \hat{\rho}_{\text{min}} > \chi, \quad (20) \]

and zero otherwise.

No level can contribute negatively to the broadening, i.e., within this framework there will be no broadening at all when \( \rho_{\text{max}} < \rho_{\text{min}} \) as determined
from Eq. (7) via (19). This is assured by requiring, somewhat artificially,

$$\rho_{\text{max}} = \text{Max}(\rho_{\text{min}}, \rho_{\text{max}}) \quad \text{and} \quad \rho_{\text{min}} = \text{Min}(\rho_{\text{min}}, \rho_{\text{max}})$$

in the "weak" and "strong" terms in Eq. (18), respectively. This maximum impact parameter may be used as long as Debye shielding gives a small reduction in the width. Otherwise, the formalism for overlapping lines (hydrogen) should be applied. 4,11,25

III. VALIDITY AND JUSTIFICATION

There is no need, at this point, to discuss criteria for all of the approximations which are involved, as many of them are treated in the literature 1,4,11 and can be accepted here without change. For any given approximation, the discussion must remain far less precise than, say, in atomic collision theory, because the integrations over angle, impact parameter and velocity (thermal average) imply such a variety of conditions that any criterion will be violated by some electrons for any given line. This makes it necessary to consider the "average perturber," bearing in mind that allowances must be made for "individuals."

When the Dyson series breaks down, higher order terms are taken into account by the strong collision correction, (which includes elastic effects). This correction to the first non-vanishing term of the Dyson expansion is the same as that used by GBKO, but they use only the first (dipole) term of the multipole expansion. Here we consider the effect of the next (quadrupole) term of the multipole expansion by examining the results implied by Section II.

We shall see that quadrupole terms are likely to be important only when $$\kappa \omega_D > kT/n^2$$, where $$\omega_D$$ is the level spacing of the closest dipole interacting level, and $$n$$ is a typical principal quantum number. This is never true for
temperatures of interest (>0.25eV) in helium, but it may be so for other elements. Even then however, the strong collision corrections will be of greater importance than the quadrupole correction.

The dipole results give two limiting cases for the minimum impact parameter \( \rho_{\text{min}} \):

Case I, \( \frac{\omega_D \rho_{\text{min}}}{\nu} < 1 \). Inelastic transitions are most important and Eqs. (7) and (10) give (making suitable estimates for the matrix elements)

\[
\rho_{\text{min}} \sim n^2 \kappa^3 \ .
\]  

(22)

Case II, \( \frac{\omega_D \rho_{\text{min}}}{\nu} > 1 \). Then collisions are adiabatic (\( A_2 = 0 \)) and from Eqs. (7) and (10)

\[
\rho_{\text{min}} \sim n^4 \kappa^2 \left( \frac{mv}{\sqrt{\omega_D}} \right)
\]

or

\[
\rho_{\text{min}} \sim n^4 \kappa^2 \left( \frac{\nu}{\rho_{\text{min}} \omega_D} \right)
\]

(23)

Since \( \kappa \omega_D < E_H / n^2 \) (i.e., the ionization energy of the level), (22) and (23) give

\[
n^2 \kappa^3 \gtrsim \rho_{\text{min}} \gtrsim n^2 \kappa^2 \left( \frac{kT}{E_H} \right)^{1/3}
\]

(24)

For \( n \gtrsim 2 \) and \( kT > 0.25eV \), we have \( \rho_{\text{min}} \gtrsim \kappa \), so usually the classical path approximation holds. Thus \( |R|/\rho \lesssim \frac{n^2 a_0}{c_{\text{min}}} \approx (kT/E_H)^{1/2} \) for case I and \( \lesssim (kT/E_H)^{1/6} \) for case II. If \( kT < E_H \), we always have \( |R|/\rho < 1 \), and so whenever the Dyson series with the dipole interaction is valid, the multipole expansion is also valid. (Atoms do not exist un-ionized if \( kT > E_H \)).

If \( \omega_0 \) is the spacing to the nearest quadrupole interacting level, we usually have \( \omega_D \rho_{\text{min}} / \nu < 1 \). We therefore have to consider two cases

(\( \varepsilon_D = \omega_D \rho_{\text{min}} / \nu > 1 \) or \( < 1 \)) as before.
If $z_D < 1$, we immediately obtain from Eq. (18) that, in the weak collision term, the ratio of quadrupole to dipole widths is

$$\frac{w_Q}{w_D} = \left( \frac{n^2 a_o}{\rho \rho_{\text{min}}} \right)^2 \times n |z_D| \ll 1 . \quad (25)$$

Here the quadrupole width is relatively unimportant (although its effect increases slightly with temperature since $(n^2 a_o/\rho_{\text{min}})^2 \sim kT/E_H$).

The case $\omega_D \rho_{\text{min}}/v > 1$ is more interesting. Using Eq. (18) with $z_Q \ll 1$ and $z_D \gg 1$, now gives for the weak collision widths:

$$\frac{w_D}{w_Q} \sim \frac{5 \pi}{2} \left( \frac{\rho_{\text{min}}}{n^2 a_o} \right)^2 e^{-2 |\omega_D \rho_{\text{min}}/v|} . \quad (26)$$

This is dominated by the exponential, so it is possible to have $w_Q > w_D$.

Under these circumstances ($z_D \gg 1$) we would determine $\rho_{\text{min}}$ from (7) and (10), now with the quadrupole contribution included. This gives

$$\frac{1}{2} \left( \frac{\chi}{\rho} \right)^2 n^4 \left[ \frac{\pi}{3} \frac{v}{\omega_D \rho} + \frac{1}{5} \left( \frac{n^2 a_o}{\rho} \right)^2 \right] \approx 1 .$$

The quadrupole term in this equation is never important. It can equal the dipole term only if $\rho < \chi/5 \frac{n^2 h \omega_D}{E_H} (< \chi/5)$, whereas we know from Eq. (24) that $\rho_{\text{min}} > \chi$ holds for temperatures of interest (otherwise the classical path approximation would break down in any case). Thus, when $z_D \gg 1$, $\rho_{\text{min}}$ is still given by Eq. (23) even when the quadrupole contribution is included.

The exponent in Eq. (26) then dominates when

$$\chi \omega_D >> \frac{kT}{n^2} . \quad (27)$$
If, however, we compare \( w_Q \) with the strong collision width \( w_S \) in these same circumstances \( (z_D > 1) \), we have from Eq. (18)

\[
\frac{w_Q}{w_S} = \frac{2}{15} n 8 \frac{a_o^{2 \chi^2}}{\rho_{\text{min}}^4},
\]

which gives, using Eq. (24):

\[
\frac{2}{15} \left( \frac{E_H/kt}{E_H} \right)^{1/3} > \frac{w_Q}{w_S} > \frac{2}{15} \frac{kt}{E_H}.
\]

Therefore, we have under all interesting circumstances \( (T > 0.25eV) \) \( w_S > w_Q \), and the effect of the strong collision correction will be more important than the quadrupole correction.

Equation (27) can never be satisfied for helium at any interesting temperature. The fact that it is possible for the quadrupole term to dominate the weak collision part of the width in other atoms (although it is expected to be small compared with the strong collision term) is our justification for including quadrupole effects in our detailed computations. These results agree with numerical computations. (As stated in the concluding paragraph of the next section, when quadrupole contributed 10%, the strong term gave 50%).

The conclusion therefore is that quadrupole effects are always smaller than strong collision corrections. There seems little point in evaluating the next (4th order) term in the Dyson expansion, because when it is important, all terms of the series will be. (So we might just as well retain the usual strong collision correction.)

It might be argued that importance of the quadrupole term implies necessarily that the octupole term is of comparable importance and that the multipole series may diverge. However, the quadrupole term is important
compared with the dipole term when the multipole series is valid only due
to the influence of $\omega_D \gg \omega_Q$ in the exponential factors. For octupole
and higher multipoles we have typically $\omega \sim \omega_Q$, so we cannot expect any
significant difference in the exponential factors and thus $w_{oct}/w_Q <\ll 1$.

It remains to discuss the matrix elements which are required in
evaluating Eqs. (7) and (18). The Coulomb approximation\textsuperscript{26} can give poor
results, not only because of marginal applicability but because the desired
matrix element may require interpolation near a zero in the table. More
sophisticated approaches to the radial matrix element are too cumbersome or
time consuming for the present purpose. A program based on the original
paper,\textsuperscript{26} but generalized to provide quadrupole matrix elements,\textsuperscript{27} has therefore been used; every matrix element is obtained from the defining equations
rather than from tables.

The angular part was always obtained by assuming LS coupling.\textsuperscript{28} Large
errors for individual matrix elements can again be expected to average out
in the summations over individual terms especially when breakdown of LS
coupling is primarily responsible. As a check, the sum rule

$$\sum_{i,i'} \frac{|\langle i|R|i'|\rangle|^2}{2(j_i + 1)} = \langle i|R^2|i\rangle \quad (28)$$

was evaluated and found to be obeyed within a few percent in all cases
where a sufficient number of levels was available.
IV. RESULTS AND DISCUSSION

Numerical calculations were carried out for a number of neutral helium lines. Helium was chosen because of its importance and because the wave functions are better known than for most neutrals. Many of the refinements which were made in the GBKO theory do not have great numerical significance in most helium lines. Other elements are therefore being considered, but their inclusion would be beyond the scope of this report.

The strong He I 5876 line was chosen as an example for a more detailed analysis of the contributions of different terms and the effect of various corrections on the width. Table I lists half halfwidths \( w \) as a function of the temperature at \( 10^{16} \) electrons/cm\(^3\), in columns 2 to 7, viz., according to GBKO, Griem\(^3,4\) the present approach (Eq. (18)), and, respectively, the three modifications: dipole only, unsymmetrized \( z \), and 1.2 in place of unity on the right hand side of Eq. (7) (Threshold used with, and only with, symmetrization).

The difference between our best value in column 4 and the earlier results arises from (probably approximately in this order of importance):

- symmetrization (not included in columns 2, 3)
- lower level broadening (not included in column 3)
- different \( \rho_{\text{min}} \) criterion (different in column 3)
- improved functions \( a_2 \) (not used in columns 2, 3)
- quadrupole interactions (not included in columns 2, 3)
- \( x \) cutoff (not used in columns 2, 3)
- different matrix elements (different in columns 2, 3).
TABLE I

He I 5876 (Half) Halfwidths w and Parameters $\alpha$

at $N_e = 10^{16}$ cm$^{-3}$

<table>
<thead>
<tr>
<th>T</th>
<th>GBKO</th>
<th>Ref. 4</th>
<th>Present</th>
<th>Dipole</th>
<th>$\Delta S = 1.2$</th>
<th>$\alpha$</th>
<th>$\alpha$ upper</th>
<th>$\alpha$ Ref. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>-</td>
<td>.162</td>
<td>.147</td>
<td>.146</td>
<td>.128</td>
<td>.152</td>
<td>.068$^5$</td>
<td>.068$^3$</td>
</tr>
<tr>
<td>5000</td>
<td>.165</td>
<td>.180</td>
<td>.159</td>
<td>.158</td>
<td>.149</td>
<td>.164</td>
<td>.064$^6$</td>
<td>.064$^4$</td>
</tr>
<tr>
<td>10000</td>
<td>.176</td>
<td>.186</td>
<td>.166</td>
<td>.165</td>
<td>.163</td>
<td>.170</td>
<td>.062$^7$</td>
<td>.062$^5$</td>
</tr>
<tr>
<td>40000</td>
<td>.180</td>
<td>.182</td>
<td>.171</td>
<td>.169</td>
<td>.173</td>
<td>.175</td>
<td>.061$^5$</td>
<td>.061$^3$</td>
</tr>
<tr>
<td>80000</td>
<td>.173</td>
<td>.172</td>
<td>.168</td>
<td>.166</td>
<td>.170</td>
<td>.172</td>
<td>.062$^3$</td>
<td>.062$^1$</td>
</tr>
</tbody>
</table>
While it is impossible to sort out how much each of these changes (hopefully improvements) contributes to the difference, it is interesting to note by how much our results change if some of these changes are not made.

Symmetrization is most noticeable at low temperatures where the threshold cutoff will be important. It will be difficult to make a decisive experiment in helium as the change it causes in the width \( w \) tends to be too small. Other atoms (e.g., Cl I) with much larger \( \omega_D \) values might provide better test cases.

It is most encouraging that an arbitrary change in the \( \rho_{\text{min}} \) cutoff (right hand side of Eq. (7)) by 20% from 1 to 1.2 changes the width not even by as much as 3% (compare columns 4 and 7). The weak and strong contributions both change by about 20%, but the increase in the weak contribution is almost completely cancelled by the decrease in the ("strong") Lorentz-Weisskopf term, which accounts for 25% of the total impact broadening in column 3. The strong collision contribution ranges from 41% at \( T = 2500^\circ\text{K} \) to 23% at \( T = 80,000^\circ\text{K} \).

The quadrupole contribution increases with temperature but is small throughout the range, because the temperature is always low enough to insure the convergence of the multipole series, but not low enough to give rise to the effect (when \( z_J \gg 1, z_Q \ll 1 \)) discussed in the previous section. The quadrupole contribution, which may be obtained by comparing columns 4 and 5, is larger than the contribution of the quadrupole term in column 4, because the inclusion of quadrupole interactions increases the strong collision term slightly. The interference term contributes only a small (negative) portion to the total quadrupole broadening (and often vanishes entirely as a consequence of the properties of the 6-j symbols).
The improved $a_2$ functions led to a reduction of the width by a fraction of a percent in helium and by at most 2% in cases where level spacings are comparable with the thermal energy, although the new functions are up to 40% smaller. The reason is that most of the contribution usually comes from $z<<1$ where $a_2(z)$ diverges logarithmically, and where the correct asymptotic form was used in GBKO and by Griem.\textsuperscript{3,4} (The improved $b_2$ functions lead to changes in the shift by typically 10% or less.)

Lower level broadening has little effect in helium where $<i|R^2|i>$ $<f|R^2|f>$. In fact, the inclusion of only the most strongly interacting configuration usually gives widths within 20% of column 4, the inclusion of more configurations changes primarily $\rho_{\text{min}}$, with large cancellations between the corresponding changes in weak and strong contributions. In one example, the total width increased by only about 25% (rather than 100%) upon inclusion of the lower level even when the broadening of upper and lower levels were equal.

The change in the width due to the $\times$ cutoff is less than 1%, which indicates once more that quantum effects are not important and the classical path approximation is applicable.

Columns 8, 9, and 10 of Table I show the quasistatic broadening parameter $\alpha$ (see Ref. 4) from

$$\alpha = \frac{4\pi}{3} N e \left[ \frac{1}{3} w \left( \frac{\kappa}{m} \right)^2 \left( \frac{R^2}{i i'} - \frac{R^2}{f f'} - \frac{R^2}{i f'} - \frac{R^2}{f i'} \right) \right]^{3/4} \quad (29)$$

from this relation without the sum over $f'$ (i.e., without regard to lower level broadening), and according to GBKO, respectively. The small effect of the lower level is here due to its small matrix elements. The difference is much more significant in many ions and the heavier neutrals.
We see that many factors which have an influence on $\rho_{\text{min}}$ fortunately have a small effect on the widths. On the other hand, $\rho_{\text{min}}$ is a more sensitive indication of various effects than is the width. Normally, the minimum angular momentum $l_{\text{min}} = \rho_{\text{min}} / \lambda$ (as function of velocity) increases from about 2.5 near $v = 10^6$ cm/sec, to more than 10 near $v = 5 \times 10^8$ cm/sec. Quadrupole effects become noticeable above $v = 10^8$ cm/sec, indicating the beginning of breakdown of the multipole expansion. In our results there is an abrupt increase (with $v$) of $l_{\text{min}}$ at the threshold for the interacting level with the smallest positive $\omega_D$. The unsymmetrized $l_{\text{min}}$ shows a very similar (though smoothed) feature at this point, while it is generally smaller at low velocities and, in fact, becomes less than unity near $2 \times 10^6$ cm/sec in violation of the classical path approximation. Since a full quantum treatment should replace the classical path approximation when $l$ is not much larger than one, it is suggestive that the need does not arise when symmetrization is used, perhaps because it is already closer to the quantum mechanical result (as found by Seaton\textsuperscript{21}).

It is difficult to define the contribution of an individual level to the width. It is not simply the corresponding term in Eq. (18), but through the Eq. (7) it has an influence on $\rho_{\text{min}}$ and thus on every other term in Eq. (18) as well. When using the former as a rough indicator, it is seen that, in general, the level with smallest $\omega_D$ (which will also have the largest matrix element in most cases) contributes most to the broadening, but that other levels become important at higher temperature. In the shift, the effects of levels with $\omega > 0$ and $\omega < 0$ are equal but opposite. In particular, a level will be shifted "up" by lower interacting levels, "down" otherwise. Since the effect of each level is weighted by its matrix element and also depends on its $\omega$ value, the total shift is usually in the direction indicated by the closest interacting level. In the width, however, all levels increase
the broadening regardless of the sign of \( \omega \). In the unsymmetrized version the amount depends only on \( |\omega| \) since \( z = \frac{|\omega|}{v} \). This is not so in the symmetrized version, where levels with \( \omega > 0 \) contribute only above threshold. Accordingly, levels with \( \omega < 0 \) contribute exclusively when \( T \to 0 \)(superelastic collisions). Note, however, that terms with \( \omega > 0 \) still affect \( \rho_{\min} \) via the unsymmetrized imaginary part of the S-matrix (B-functions).

Table II illustrates the effect for the strongest interacting levels with \( \omega > 0 \) and \( \omega < 0 \) of the He I 5876 line. The unsymmetrized contribution in parentheses is given for comparison, also, its variation with temperature illustrates the effect of levels with different value of \( |\omega| \) but with the same sign.

Table III gives the half halfwidth \( w \) and the quasistatic parameter \( a \) for the He I 5016 line as functions of temperature and density. The line was chosen because it exhibits Debye shielding at comparatively low electron density while being easily observable. Most of the shielding (deviation from linearity with electron density \( N_e \)) occurs on the "weak" contribution of the closest interacting levels. The effect on strong collisions is small since they are close collisions \( (\rho < \rho_{\min}) \). The prescription for \( \rho_{\min} \) in the second Eq. (21) has no noticeable effect.

It has been pointed out in the introduction that recent work\(^19\) proposes that both fields in the autocorrelation function (see appendix of GBKO) should be shielded. This would change the equivalent cutoff from 1.123 \( \rho_D \) to .68 \( \rho_D \) in the \( v \to \infty(z \to 0) \) limit. In hydrogen \( (\omega = 0) \) the equivalent cutoff is correct at all velocities \( v \), however, in helium (and for all isolated lines) it is valid only in the high velocity limit \( (z \ll 1) \), and since most shielding occurs at low velocities it is probably a poor approximation anyhow whenever \( z \sim 1 \).

Since an analytic treatment of \( A, a \) and corresponding numerical computation of \( B, b \) are possible, the need for a cutoff is eliminated entirely. Results will be given in a subsequent paper.
TABLE II

Contribution of Individual Levels to the "Weak" Impact Width of He I 5876 at
\( N_e = 10^{16} \text{ cm}^{-3} \)

<table>
<thead>
<tr>
<th>( R_{ii}^2 [a_o^2] )</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Temperature [°K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega [1/\text{sec}] )</td>
<td>-10^{14}</td>
<td>+10^{15}</td>
<td>-</td>
</tr>
</tbody>
</table>

Contributions in % of "weak" impact width:
- Contribution: 99.7 (99.6); 0.06 (0.41); 2500
- in % of "weak" impact width: 99 (98); 0.7 (1.85); 5000
- unsymmetrized values in parentheses: 96 (94); 3.4 (5.5); 10000
- unsymmetrized values in parentheses: 89 (87); 9.4 (11.7); 20000
- unsymmetrized values in parentheses: 79 (77); 17.5 (19.2); 40000
- unsymmetrized values in parentheses: 68 (67); 25 (26); 80000
TABLE III

Half Halfwidths w, and Quasistatic

Broadening Parameters $\alpha$ for Neutral Helium Multiplet 4.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$K)</th>
<th>Electrons/cm$^3$</th>
<th>$10^{15}$</th>
<th>$10^{16}$</th>
<th>$10^{17}$</th>
<th>$10^{18}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2500</td>
<td>w (Å)</td>
<td>0.0382</td>
<td>0.378</td>
<td>3.20</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.0854</td>
<td>0.153</td>
<td>0.309</td>
<td>1.00</td>
</tr>
<tr>
<td>5000</td>
<td>w (Å)</td>
<td>0.0377</td>
<td>0.371</td>
<td>3.31</td>
<td>20.6</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.0864</td>
<td>0.155</td>
<td>0.301</td>
<td>0.763</td>
</tr>
<tr>
<td>10000</td>
<td>w (Å)</td>
<td>0.0355</td>
<td>0.353</td>
<td>3.25</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.0888</td>
<td>0.161</td>
<td>0.305</td>
<td>0.686</td>
</tr>
<tr>
<td>20000</td>
<td>w (Å)</td>
<td>0.0332</td>
<td>0.331</td>
<td>3.09</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.0903</td>
<td>0.169</td>
<td>0.317</td>
<td>0.665</td>
</tr>
<tr>
<td>40000</td>
<td>w (Å)</td>
<td>0.0311</td>
<td>0.309</td>
<td>2.88</td>
<td>24.5</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.0866</td>
<td>0.178</td>
<td>0.334</td>
<td>0.671</td>
</tr>
<tr>
<td>80000</td>
<td>w (Å)</td>
<td>0.0296</td>
<td>0.294</td>
<td>2.65</td>
<td>23.3</td>
</tr>
<tr>
<td></td>
<td>$\alpha$</td>
<td>0.0862</td>
<td>0.185</td>
<td>0.355</td>
<td>0.696</td>
</tr>
</tbody>
</table>
It has been shown recently (J. R. Greig and H. R. Griem, private communication) that a reduction of the width to electron density ratio can also result by the excitation of forbidden components as the line is no longer strictly isolated. This effect competes with Debye shielding and a full treatment should include both effects. (Under these conditions Eqs. (29) and (1) also are not valid.)

Table IV lists \( w \) and \( \alpha \) for a number of He I multiplets. They were computed at various electron densities and scaled to \( 10^{16} \text{ cm}^{-3} \). Generally, the agreement with earlier results\(^4\) is good, as expected for helium.

As an example, for the application of the present method to a heavier atom it may be in order to consider a chlorine line for which preliminary experimental results\(^{29}\) indicate more broadening than previously predicted.\(^4\) Preliminary computations for Cl I multiplet 5 at \( T = 12,000 \text{K} \), where the level spacing is large compared to the thermal energy, indicate that the width is larger than previously computed by a factor \( \sim 2 \). However, we notice that quantum defects are very large, and that the sum rules are violated by factors \( \sim 2 \), i.e., the sum is less than \( \langle i | R^2 | i \rangle \). Thus the width would be still larger if proper matrix elements were used.\(^*\) We also notice that strong collisions contribute about 50% to the width. Weak dipole and quadrupole collisions contribute 40% and 10%, respectively. The quadrupole contribution increases with decreasing temperature, i.e., in the range where the multipole expansion converges. More complete tables of widths and shifts for many of the elements are in preparation.

\(^*\) This contention was proved by Roberts\(^{30}\) who included additional levels (primarily 3d configuration) which were found by Humphreys and Paul.\(^{31}\) Roberts used the GbKO theory without the present additions and found that the discrepancy between predicted and measured width decreased from an order of magnitude to slightly less than a factor of two as a result of inclusion of the levels. Roberts' other improvements in the theory proved to be much less important, except for the inclusion of lower level broadening. We can show that the sum of matrix elements with LS coupling and within the Coulomb approximation exceeds the sum rule value when the additional levels are included. However, the width predicted by the present theory including the additional levels still falls short of the measured width by a factor of order two. This is due to the unusually large contribution of strong collisions to the width (\( \sim 70\% \)) and possibly the matrix elements.
TABLE IV

Half Halfwidths \( \lambda (\text{Å}) \) and Quasistatic Broadening Parameters \( \alpha \) for some Neutral Helium Multiplets

at \( N_e = 10^{16} \text{ cm}^{-3} \).

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>2500</th>
<th>5000</th>
<th>10000</th>
<th>20000</th>
<th>40000</th>
<th>80000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multiplet 1 ( \lambda = 10832.1 )</td>
<td>w 0.0352</td>
<td>0.0362</td>
<td>0.0436</td>
<td>0.0596</td>
<td>0.0810</td>
<td>0.1010</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.0355</td>
<td>0.0347</td>
<td>0.0302</td>
<td>0.0239</td>
<td>0.0190</td>
<td>0.0161</td>
</tr>
<tr>
<td>Multiplet 2 ( \lambda = 3889.7 )</td>
<td>w 0.0729</td>
<td>0.0916</td>
<td>0.1059</td>
<td>0.1146</td>
<td>0.1194</td>
<td>0.1243</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.0963</td>
<td>0.0812</td>
<td>0.0728</td>
<td>0.0686</td>
<td>0.0665</td>
<td>0.0646</td>
</tr>
<tr>
<td>Multiplet 3 ( \lambda = 3188.7 )</td>
<td>w 0.2440</td>
<td>0.2950</td>
<td>0.3300</td>
<td>0.3480</td>
<td>0.3590</td>
<td>0.3670</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.1625</td>
<td>0.1411</td>
<td>0.1298</td>
<td>0.1247</td>
<td>0.1217</td>
<td>0.1196</td>
</tr>
<tr>
<td>Multiplet 5 ( \lambda = 3965.9 )</td>
<td>w 1.0480</td>
<td>1.0230</td>
<td>0.9620</td>
<td>0.8870</td>
<td>0.8190</td>
<td>0.8030</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.2733</td>
<td>0.2783</td>
<td>0.2915</td>
<td>0.3100</td>
<td>0.3288</td>
<td>0.3338</td>
</tr>
<tr>
<td>Multiplet 10 ( \lambda = 7067.7 )</td>
<td>w 0.1010</td>
<td>0.1320</td>
<td>0.1780</td>
<td>0.2260</td>
<td>0.2680</td>
<td>0.2950</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.1037</td>
<td>0.0851</td>
<td>0.0680</td>
<td>0.0568</td>
<td>0.0501</td>
<td>0.0465</td>
</tr>
<tr>
<td>Multiplet 11 ( \lambda = 5877.6 )</td>
<td>w 0.1470</td>
<td>0.1590</td>
<td>0.1660</td>
<td>0.1690</td>
<td>0.1710</td>
<td>0.1680</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.0685</td>
<td>0.0646</td>
<td>0.0627</td>
<td>0.0617</td>
<td>0.0615</td>
<td>0.0623</td>
</tr>
<tr>
<td>Multiplet 12 ( \lambda = 4714.7 )</td>
<td>w 0.2000</td>
<td>0.2610</td>
<td>0.3370</td>
<td>0.4060</td>
<td>0.4460</td>
<td>0.4530</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.1721</td>
<td>0.1406</td>
<td>0.1161</td>
<td>0.1011</td>
<td>0.0941</td>
<td>0.0931</td>
</tr>
<tr>
<td>Multiplet 46 ( \lambda = 6681.5 )</td>
<td>w 1.7370</td>
<td>1.5900</td>
<td>1.4190</td>
<td>1.2410</td>
<td>1.0700</td>
<td>0.9090</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.5765</td>
<td>0.6160</td>
<td>0.6708</td>
<td>0.7416</td>
<td>0.8292</td>
<td>0.9366</td>
</tr>
<tr>
<td>Multiplet 48 ( \lambda = 4923.3 )</td>
<td>w 0.1900</td>
<td>0.2060</td>
<td>0.2160</td>
<td>0.2220</td>
<td>0.2250</td>
<td>0.2220</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>0.0676</td>
<td>0.0636</td>
<td>0.0615</td>
<td>0.0602</td>
<td>0.0596</td>
<td>0.0603</td>
</tr>
<tr>
<td>Multiplet 51 ( \lambda = 4389.4 )</td>
<td>w 4.2000</td>
<td>3.9110</td>
<td>3.5120</td>
<td>3.0660</td>
<td>2.6190</td>
<td>2.1960</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>1.0169</td>
<td>1.0727</td>
<td>1.1628</td>
<td>1.2875</td>
<td>1.4492</td>
<td>1.6537</td>
</tr>
</tbody>
</table>
APPENDIX A: STARK BROADENING FUNCTIONS

From the definition\textsuperscript{1,4,11}

\[ A + iB = \int_{-\infty}^{\infty} \int_{-\infty}^{x_1} dx_1 \int_{-\infty}^{x_2} dx_2 \, e^{iz(x_1-x_2)} f(x_1, x_2) \] \hspace{1cm} (A-1)

with

\[ f_2(x_1, x_2) = \frac{1}{2} \frac{1 + x_1 x_2}{(1 + x_1^2)^{3/2}(1 + x_2^2)^{3/2}} \] \hspace{1cm} (A-2)

and

\[ f_4(x_1, x_2) = \frac{2(1 + x_1^2)(1 + x_2^2) - 3(x_1 - x_2)^2}{(1 + x_1^2)^{5/2}(1 + x_2^2)^{5/2}} \] \hspace{1cm} (A-3)

the real part \( A(z) \) can be obtained with the aid of the integral relation

\[ \int_{-\infty}^{y} f(x_1) dx_1 \int_{-\infty}^{x_1} f(x_2) dx_2 \cdots \int_{-\infty}^{x_{n-1}} f(x_n) dx_n = \frac{1}{n!} \left[ \int_{-\infty}^{y} f(x) dx \right]^n \] \hspace{1cm} (A-4)

i.e., it can be expressed\textsuperscript{1,22,23} in terms of modified Bessel functions of the second kind\textsuperscript{32} as

\[ A_2(z) = z^2 [K^2_0(|z|) + K^2_1(|z|)] \] \hspace{1cm} (A-5)

and

\[ A_4(z) = \frac{z^4}{3} \left[ K^2_2(|z|) + 4K^2_3(|z|) + 3K^2_0(|z|) \right] \] \hspace{1cm} (A-6)

Their asymptotic behavior is for large \( z \):

\[ A_2(|z|) \rightarrow |z|^{-2} |z|; \quad A_4(z) \rightarrow \frac{4z^2}{3} A_2(z) \] \hspace{1cm} with \( z \rightarrow \infty \).

Also: \( A_2(0) = 1; \quad A_4(0) = \frac{4}{3} \).
The function $a_n(z)$, defined by

$$a_n(z) = \int_0^\infty \frac{A_n(z')dz'}{z(z')^{n-1}},$$

can be expressed analytically as

$$a_2(|z|) = -|z| K_0(|z|) K_1(|z|),$$  \hspace{1cm} (A-7)

and

$$a_4(|z|) = \frac{2}{3} K_1(|z|) \left[ 2|z|K_0(|z|) + K_1(|z|) \right],$$  \hspace{1cm} (A-8)

in terms of the same kind of Bessel functions. The values given for $a_2$ in GBKO do not agree with this result (see Table V) except at the asymptotic limits:

$$a_2(|z|) \rightarrow \frac{\pi}{2} e^{-2|z|}; \quad a_4(z) \rightarrow \frac{4}{3} a_2(z); \quad z \gg 1$$

and

$$a_2(|z|) \rightarrow - \log |z|; \quad a_4(z) \rightarrow \frac{2}{3z^2}; \quad z \ll 1$$

The application of symmetry arguments which led to these results fails for the imaginary part of Eq. (A-1), and one must, in general, compute $B(z)$ from a dispersion relation, making use of the fact that $A$ and $B$ are real and imaginary parts of the same complex function (where P.V. indicates principal value):

$$B(z) = \frac{2z}{\pi} \text{ P.V.} \int_0^\infty \frac{A(z')dz'}{z^2(z^2 - z'^2)}.$$  \hspace{1cm} (A-9)

This can be brought into a manageable form for numerical evaluation by two partial integrations:

$$B(z) = \frac{1}{\pi} \int_0^\infty dz' \left[ (z-z') \log |z-z'| + (z + z') \log |z + z'| \right] \frac{d^2A(z')}{dz'^2}. \quad (A-10)$$
TABLE V

Functions $A(z)$, $a(z)$ for Dipole and Quadrupole Broadening.

<table>
<thead>
<tr>
<th>$z$</th>
<th>$A_2(z)$</th>
<th>$a_2(z)$</th>
<th>$A_4(z)$</th>
<th>$a_4(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.030</td>
<td>2.392</td>
<td>1.340</td>
<td>67.92</td>
</tr>
<tr>
<td>0.2</td>
<td>1.035</td>
<td>1.674</td>
<td>1.361</td>
<td>17.43</td>
</tr>
<tr>
<td>0.4</td>
<td>0.9622</td>
<td>0.9738</td>
<td>1.431</td>
<td>4.479</td>
</tr>
<tr>
<td>0.6</td>
<td>0.8287</td>
<td>0.6078</td>
<td>1.504</td>
<td>1.942</td>
</tr>
<tr>
<td>0.8</td>
<td>0.6799</td>
<td>0.3897</td>
<td>1.547</td>
<td>1.015</td>
</tr>
<tr>
<td>1.0</td>
<td>0.5396</td>
<td>0.2534</td>
<td>1.540</td>
<td>0.5794</td>
</tr>
<tr>
<td>1.2</td>
<td>0.4181</td>
<td>0.1661</td>
<td>1.484</td>
<td>0.3474</td>
</tr>
<tr>
<td>1.4</td>
<td>0.3181</td>
<td>0.1094</td>
<td>1.386</td>
<td>0.2146</td>
</tr>
<tr>
<td>1.6</td>
<td>0.2387</td>
<td>7.237x10^{-2}</td>
<td>1.259</td>
<td>0.1351</td>
</tr>
<tr>
<td>1.8</td>
<td>0.1771</td>
<td>4.797x10^{-2}</td>
<td>1.116</td>
<td>8.620x10^{-2}</td>
</tr>
<tr>
<td>2.0</td>
<td>0.1302</td>
<td>3.186x10^{-2}</td>
<td>0.9684</td>
<td>5.553x10^{-2}</td>
</tr>
<tr>
<td>3.0</td>
<td>2.537x10^{-2}</td>
<td>4.185x10^{-3}</td>
<td>0.3741</td>
<td>6.655x10^{-3}</td>
</tr>
<tr>
<td>4.0</td>
<td>4.486x10^{-3}</td>
<td>5.572x10^{-4}</td>
<td>0.1109</td>
<td>8.469x10^{-4}</td>
</tr>
<tr>
<td>5.0</td>
<td>7.496x10^{-4}</td>
<td>7.465x10^{-5}</td>
<td>0.02802</td>
<td>1.104x10^{-4}</td>
</tr>
</tbody>
</table>
Cancellations tend to make numerical evaluation of this integral troublesome for \( z \gg 1 \). By direct partial integration of the right side of Eq. (A-1) one obtains the asymptotic expansion (which should be terminated at the minimum term)

\[
B(z) = \sum_{n=1}^{k} c_n z^{-n} \quad (n \text{ odd}) , \tag{A-11}
\]

where

\[
c_n = \int_{-\infty}^{\infty} \left| \frac{d^{n-1}f(x_1,x_2)}{d x_2^{n-1}} \right|_{x_2=x_1} d x_1 \tag{A-12}
\]

can be found after some algebra; for the dipole case results

\[
c_{2n} = \frac{\pi}{2} \prod_{j=0}^{n-1} (2j+1) \sum_{i=1}^{n} \left( d_{i-1} \right) \frac{2n-i}{2} \prod_{j=1}^{n-i} \left( 1 - \frac{1}{2j} \right) \prod_{j=1}^{n-i} \left( 2n+2j-1 \right) \\
\times \prod_{j=1}^{i-1} (n-j) \cdot \frac{1}{n-i+1} \cdot \left[ n - \frac{1}{2} \frac{i-1}{2n-i+1}, \right], \tag{A-13}
\]

where any product for which \( j < 1 \) should be set equal to one.

Similarly, the coefficients for the quadrupole case may be obtained (with the same provision for \( j < 1 \)) from:

\[
c_{4n} = \frac{\pi}{2} \prod_{j=1}^{n-1} (2j+1) \sum_{i=1}^{n} \left( d_{i-1} \right) \frac{2n-i-1}{2} \prod_{j=1}^{n-i-1} \left( 1 - \frac{1}{2j} \right) \prod_{j=1}^{n-i} \left( 2n+2j+1 \right) \prod_{j=1}^{n-i+1} \left( n-j+1 \right) \prod_{j=1}^{2n-i+1} \left( 1 - \frac{1}{2j} \right) \\
\left\{ \frac{(2n+1)(4n-2i+3)}{(2n-i+3)(2n-i+2)} \left( \frac{[n+1][2n-i+2]}{[n+i+2]} + [4n-2i+1] \right) - \frac{[2n+1][4n-2i+3]}{[4n-2i+1][2n+i+2]} \right\}. \tag{A-14}
\]

The expressions in \([\cdot]\) equal one if \( n-i < 2 \).
The first few coefficients are listed in Table VI. The asymptotic form gives $B_2(5) \approx .1664$, Eq. (A-9) yields .1660 in good agreement, i.e., $B_2$ from (A-10) works for $z > 5$ with satisfactory precision ($k=9$). The quadrupole function is $B_4(10) \approx .2466$ (from (A-10) with $k=9$), $B_4(10) = .2438$ (from (A-9)). The latter value may not be better than the former, because large cancellations seem to occur in the integral. Numerical values for $B_2$ and $B_4$ are listed in Table VII, they were obtained from Eq. (A-10) for $z > z_1$; from Eq. (A-9) for $z \leq z_1$, with $z_1 = 5$ for $B_2$, $z_1 = 10$ for $B_4$. For $B_2$, they agree very well with results obtained by E. Corinaldesi (private communication) for $z < 5$.

<table>
<thead>
<tr>
<th>TABLE VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coefficients for the Asymptotic Expansions of</td>
</tr>
<tr>
<td>the Functions $B_2$ and $B_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_{2n}$</td>
<td>.7854</td>
<td>.8836</td>
<td>4.142</td>
<td>42.28</td>
<td>750.4</td>
</tr>
<tr>
<td>$c_{4n}$</td>
<td>2.356</td>
<td>-43.41</td>
<td>2632</td>
<td>-2.345x10^5</td>
<td>3.046x10^7</td>
</tr>
</tbody>
</table>

The functions $b_n(z) = \int_0^\infty \frac{B_n(z')}{z(z')^{n-1}} dz'$ are now easily obtained numerically, i.e., for $z > z_1$ the asymptotic form

$$b_m(z) = \sum_{n=1}^{k} \frac{c_n}{(n+m-2)z^{n+m-2}} ; \ m=2,4$$ (A-15)
with \( k = 5 \) and the \( c_n \) in Table VI may be used. For \( z < z_1 \) it is necessary to integrate numerically over the \( B \) function:

\[
b_m(z) = \int_{z}^{z_1} \frac{B_m(z')dz'}{(z')^{m-1}} + b_m(z_1) \quad . \quad (A\-16)\]

The resulting numbers are also listed in Table VII, they differ by up to 20% from the values in GBKO. A most valuable check is provided by the value \( b(o) \) obtained from Eq. (A-1) by interchanging the integrations over \( x_1 \) and \( x_2 \) with that over \( z' \), setting \( z = 0 \). This yields \( b_2(o) = \frac{\pi}{2} \) and \( b_4(o) = \frac{1}{3} \pi \). This limit was used in the table at \( z = 0 \); it is approached smoothly by the computed values as \( z \to 0 \). This gives a considerable degree of confidence for the \( B \)'s and \( b \)'s over the entire range; they should be accurate at least within better than 1%. The function \( B_2(z) \) in GBKO is numerically correct within a fraction of one percent.
### TABLE VII

Functions $b(z)$, $B(z)$ for Dipole and Quadrupole Broadening

<table>
<thead>
<tr>
<th>$z$</th>
<th>$B_2(z)$</th>
<th>$b_2(z)$</th>
<th>$B_4(z)$</th>
<th>$b_4(z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>1.5708</td>
<td>0</td>
<td>1.047</td>
</tr>
<tr>
<td>0.1</td>
<td>5.8501x10^{-2}</td>
<td>1.5295</td>
<td>5.781x10^{-4}</td>
<td>1.043</td>
</tr>
<tr>
<td>0.2</td>
<td>1.6039x10^{-1}</td>
<td>1.4577</td>
<td>6.134x10^{-3}</td>
<td>0.9539</td>
</tr>
<tr>
<td>0.4</td>
<td>3.5887x10^{-1}</td>
<td>1.2838</td>
<td>5.200x10^{-2}</td>
<td>0.7822</td>
</tr>
<tr>
<td>0.6</td>
<td>4.9819x10^{-1}</td>
<td>1.1103</td>
<td>0.1560</td>
<td>0.6256</td>
</tr>
<tr>
<td>0.8</td>
<td>5.7597x10^{-1}</td>
<td>9.5538x10^{-1}</td>
<td>0.3070</td>
<td>0.4928</td>
</tr>
<tr>
<td>1.0</td>
<td>6.0588x10^{-1}</td>
<td>8.2313x10^{-1}</td>
<td>0.4806</td>
<td>0.3849</td>
</tr>
<tr>
<td>1.2</td>
<td>6.0315x10^{-1}</td>
<td>7.1258x10^{-1}</td>
<td>0.6528</td>
<td>0.2994</td>
</tr>
<tr>
<td>1.4</td>
<td>5.8021x10^{-1}</td>
<td>6.2115x10^{-1}</td>
<td>0.8052</td>
<td>0.2327</td>
</tr>
<tr>
<td>1.6</td>
<td>5.4590x10^{-1}</td>
<td>5.4586x10^{-1}</td>
<td>0.9274</td>
<td>0.1810</td>
</tr>
<tr>
<td>1.8</td>
<td>5.0663x10^{-1}</td>
<td>4.8382x10^{-1}</td>
<td>1.015</td>
<td>0.1412</td>
</tr>
<tr>
<td>2.0</td>
<td>4.6692x10^{-1}</td>
<td>4.3251x10^{-1}</td>
<td>1.069</td>
<td>0.1106</td>
</tr>
<tr>
<td>3.0</td>
<td>3.0540x10^{-1}</td>
<td>2.7638x10^{-1}</td>
<td>0.9975</td>
<td>3.600x10^{-2}</td>
</tr>
<tr>
<td>4.0</td>
<td>2.1580x10^{-1}</td>
<td>2.0212x10^{-1}</td>
<td>0.7516</td>
<td>1.432x10^{-2}</td>
</tr>
<tr>
<td>5.0</td>
<td>1.6640x10^{-1}</td>
<td>1.5978x10^{-1}</td>
<td>0.5618</td>
<td>6.889x10^{-3}</td>
</tr>
<tr>
<td>6.0</td>
<td>1.3575x10^{-1}</td>
<td>1.3240x10^{-1}</td>
<td>0.4416</td>
<td>3.818x10^{-3}</td>
</tr>
<tr>
<td>7.0</td>
<td>1.1509x10^{-1}</td>
<td>1.1312x10^{-1}</td>
<td>0.3646</td>
<td>2.331x10^{-3}</td>
</tr>
<tr>
<td>8.0</td>
<td>1.0005x10^{-1}</td>
<td>9.8779x10^{-2}</td>
<td>0.3119</td>
<td>1.522x10^{-3}</td>
</tr>
<tr>
<td>9.0</td>
<td>8.8559x10^{-2}</td>
<td>8.7686x10^{-2}</td>
<td>0.2734</td>
<td>1.041x10^{-3}</td>
</tr>
<tr>
<td>10.0</td>
<td>7.9470x10^{-2}</td>
<td>7.8843x10^{-2}</td>
<td>0.2438</td>
<td>7.378x10^{-4}</td>
</tr>
</tbody>
</table>
APPENDIX B: ANGULAR AVERAGING

One convenient way to obtain the angular average for the quantity

\[ \langle 1 - |S| \rangle \langle f | S^{-1} | f \rangle \] \[ \text{AV} \]

is as follows. One picks a simple set of axes—the collision axes—to calculate the S-matrix for a collision (for example, take the z-axes along the impact parameter). Denote the S-matrix referred to these axes by \( S_c \). In order to transform the fixed atomic axes into these collision axes, a rotation through Euler angles \( \alpha, \beta, \gamma = \Omega \) has to be performed.

Denoting states of the atom by \( |\gamma J M\rangle \) where \( J \) is the total angular momentum, in this rotation the wave functions transform as follows

\[ D(\Omega) |\gamma J M\rangle = \sum_{M_1 M_2 M_1'} \mathcal{D}_{M_1 M_2}^{(J)}(\Omega) |\gamma J M\rangle \] \[ (B-1) \]

Since collisions occur at random directions with respect to fixed atomic axes, the final angular average is obtained by averaging over all \( \alpha, \beta, \gamma \).

The result of the average can be written in terms of 3-j symbols as

\[ \langle 1 - |S| \rangle \langle f | S^{-1} | f \rangle \] \[ \text{AV} = 1 - \sum_{M_1 M_2 M_1'} (-1)^{J_f + M_1' + M_1} \begin{vmatrix} J_f & 1 & J_i & 1 \\ M_f & m - M_f & M_2 & m - M_1 \end{vmatrix} \begin{vmatrix} J_f & 1 & J_i & 1 \\ M_f & m - M_f & M_2 & m - M_1 \end{vmatrix} \langle J_i M_1' | S_c | J_i M_1 \rangle \times \langle J_f M_2 | S^{-1}_c | J_f M_1' \rangle \] \[ (B-2) \]

Using the second order expansion for S-matrix elements, we find

\[ \langle F_{fi} \rangle = 1 - \sum_{M_f, M_i, M_1} (-1)^{2J_f + M_f + M_i} \begin{vmatrix} J_f & 1 & J_i & 1 \\ M_f & m - M_f & M_2 & m - M_1 \end{vmatrix} \begin{vmatrix} J_f & 1 & J_i & 1 \\ M_f & m - M_f & M_2 & m - M_1 \end{vmatrix} \langle J_i M_1 | S_c | J_i M_1 \rangle \]

\[ = \frac{1}{(2J_i + 1)} \sum_{M_1} \langle J_i M_1 | \int_{-\infty}^{t_1} dt_1 \int_{-\infty}^{t_2} dt_2 V(t_1) V(t_2) | J_i M_1 \rangle, \] \[ (B-3) \]

where we have used the orthogonality properties of the 3-j symbols and

\[ \langle J_f M_f | J_i M_2 \rangle = \delta(M_f, M_2) \]. Similarly for \( \langle F_{ff} \rangle \),
\[
\langle F_{ff} \rangle = \frac{1}{(2J_f+1)} \sum_{J_{1f}, M_{1f}} \int_{-\infty}^{\infty} \int_{-\infty}^{t_1} \int_{-\infty}^{t_2} \tilde{V}(t_1) \tilde{V}(t_2) | J_{1f} M_{1f} \rangle < J_{1f} M_{1f} | J_{1f} M_{1f} >. \quad (B-4)
\]

The interference term is
\[
\langle F_{ij} \rangle = \sum_{J_{11}, M_{11}} \sum_{J_{12}, M_{12}} \left( \begin{array}{ccc} J_f & 1 & M_{11} \\ M_{1f} & m & -M_{1f} \end{array} \right) \left( \begin{array}{ccc} J_f & 1 & J_1 \\ M_2 & m & -M_1 \end{array} \right) \langle J_{i1} M_{i1} | \int_{-\infty}^{\infty} V(t) dt | J_{i1} M_{i1} \rangle < J_{i1} M_{i1} | \int_{-\infty}^{\infty} V(t) dt | J_{i1} M_{i1} \rangle \quad (B-5)
\]

using the fact that \( \langle J_{i1} M_{i1} | \int_{-\infty}^{\infty} V(t) dt | J_{i1} M_{i1} \rangle = \langle J_{i1} M_{i1} | \int_{-\infty}^{\infty} V(t) dt | J_{i1} M_{i1} \rangle \) etc. It is most convenient for the interference term to expand \( \int_{-\infty}^{\infty} V(t) dt \) in terms of tensor operators \( \mathcal{C}^{(k)}_{q} = (4\pi/2k+1)^{1/2} Y_{kq} \), where \( Y_{kq} \) is a spherical harmonic,

i.e., put \( \int_{-\infty}^{\infty} V(t) dt = \sum_{k, q} a_{q} \mathcal{C}^{(k)}_{q} R^{k} \quad (B-6) \)

so that
\[
\langle J_{i1} M_{i1} | \int_{-\infty}^{\infty} V(t) dt | J_{i1} M_{i1} \rangle = \sum_{k, q} a_{q} (-1)^{k+1} \left( \begin{array}{ccc} J_i & k & J_f \\ -M_i & q & M_f \end{array} \right) (J_{i} || R^{k} C(k) || J_{f}) \quad (B-7)
\]

where \( (J_{f} || R^{k} C(k) || J_{f}) \) is a reduced matrix element. Then in terms of a 6-j symbol the interference term is
\[
\langle F_{ij} \rangle = \sum_{k, q} \left( \begin{array}{ccc} J_i + J_f + 1 & J_i & J_f \\ J_{i1} & 1 & J_{i1} \end{array} \right) (-1)^{k+q} a_{q} a_{k} \left( \begin{array}{ccc} J_i & k & J_f \\ -M_i & q & M_f \end{array} \right) (J_{i} || R^{k} C(k) || J_{i}) (J_{f} || R^{k} C(k) || J_{f}) \quad (B-8)
\]

Notice that if we had retained first order terms they would have vanished on the angular average.

For calculating \( \langle F_{ii} \rangle \), \( \langle F_{ff} \rangle \), and \( \langle F_{ij} \rangle \) we use the first two terms for the multipole expansion and take collision axes such that the impact parameter is in the z-direction and \( v \) is in the x-direction. For a straight line path \( \mathbf{r} = \mathbf{r}_0 + \mathbf{v} t \), and for the atomic coordinates \( x, y, z \) (with \( R^2 = x^2 + y^2 + z^2 \)) this gives, using Eq. (9), \( V(t) = V(2) (t) + V(4) (t) \) where
\[ V^{(2)}(t) = e^{2R[vt/\sqrt{v}]} (C_{-1}^1 - C_{+1}^1 + \rho C_{0}^1)/(\rho^2 + v^2 t^2)^{3/2} \]  \hspace{1cm} (B-9)

and \[ V^{(4)}(t) = \frac{e^{2R^2}}{2} \sqrt{\frac{3}{2}} \left[ v^2 t^2 (C_{+2}^2 + C_{-2}^2) - 2\rho vt(C_{+2}^2 - C_{-2}^2) - \frac{\sqrt{2}}{3} (v^2 t^2 - 2\rho^2) C_{0}^0 \right] \left( \frac{v^2 t^2 + \rho^2}{\rho^2 + v^2 t^2} \right)^{5/2} \]  \hspace{1cm} (B-10)

Substitution in Eqs. (B-3) and (B-4) gives \( <F_{ii}> = <F^{(2)}_{ii}> + <F^{(4)}_{ii}> \) etc.

Notice that there is no mixing between dipole and quadrupole terms since the dipole selection rule for the "jumping electron" is \( \Delta \ell = \pm 1 \), but is \( \Delta \ell = 0, \pm 2 \) for quadrupole terms.

Substitution of \( V^{(2)}(t) \), using orthogonality relations for the 3-\( J \) symbols and \( <J_{1} M_{1}|V(t)|J_{k} M_{k}> = e^{i(E_{1} - E_{k})t/\hbar} \), gives

\[ <F^{(2)}_{ii}> = \frac{e^2}{3(2J_{i} + 1)} \sum_{J_{k}} \left( (J_{1} R C_{1})(|J_{k}|) \right)^2 \int_{-\infty}^{\infty} dt_{1} \int_{-\infty}^{t_{1}} dt_{2} e^{i\omega_{ik}(t_{1}-t_{2})} \left[ \frac{v^2 t_{1} t_{2} + \rho^2}{(\rho^2 + v^2 t_{1}^2)^{3/2}} \right] \left( \frac{\rho^2 + v^2 t_{2}^2}{(\rho^2 + v^2 t_{2}^2)^{3/2}} \right)^{3/2} \]

\[ = \frac{2}{3} \frac{\hbar^2}{m_{p} v} \sum_{J_{k}} \frac{(J_{1} R C_{1})(|J_{k}|)}{(2J_{i} + 1)} \left[ A_{2}(z_{ik}) + i B_{2}(z_{ik}) \right] \]  \hspace{1cm} (B-11)

where \( \omega_{ik} = \frac{E_{i} - E_{k}}{\hbar} \), \( z_{ik} = \frac{\omega_{ik}}{v} \), \( x = vt/\rho \) and \( \hat{R} \) matrix elements are in units of \( a_{0} \). The \( <F^{(2)}_{ff}> \) is equivalent except that the \( B \) term is negative due to the fact that we have \( S_{-1}^{1} \) instead of \( S_{c}^{1} \). This is exactly what we would expect since the \( B \) part corresponds to a line shift, and shifts of the upper and lower states in the same direction will tend to cancel. For the \( <F^{(4)}_{ii}> \) we get by the same procedure

\[ <F^{(4)}_{ii}> = \frac{e^4}{10(\rho^2 v^2)^2} \sum_{J_{k}} \frac{(J_{1} R C_{1})(2)(|J_{k}|)}{(2J_{i} + 1)} \int_{-\infty}^{\infty} dx_{1} \int_{-\infty}^{x_{1}} dx_{2} e^{iz_{ik}(x_{1}-x_{2})} \left[ \frac{2(x_{1}^2 + x_{2}^2) - 3(x_{1} - x_{2})^2}{(1+x_{1}^2)^{5/2}} \frac{(1+x_{2}^2)^{5/2}}{(1+x_{2}^2)^{5/2}} \right] \]
\[
\frac{a^2}{10} \left( \frac{\hbar^2}{m} \right)^2 \frac{1}{\rho v^2} \sum_{J_k} \frac{(J_\| R^2 C(2) \| J_k)^2}{(2J_\| +1)} \left[ A_4(z_{1k}) + iB_4(z_{1k}) \right]. \quad (B-12)
\]

The \( F_{ff}^{(4)} \) is equivalent but with a negative \( B \) term.

Finally, Eqs. (B-9) and (B-10) can be integrated as in (B-6) to obtain the coefficients \( a^k \) necessary for the interference term. However, since in Eq. (B-8) we have reduced matrix elements between the same state, the dipole term vanishes since we cannot satisfy the \( \Delta \lambda = \pm 1 \) (parity) selection rule. The quadrupole term is easily computed to be

\[
\langle F_{if}^{(4)} \rangle = \frac{4}{15} (-1)^{J_\| + J_f - 1} \left( \frac{a^2}{\rho \ h^2} \right)^2 \left\{ \begin{array}{c} J_\| & 2 & J_\| \\ J_f & 1 & J_f \end{array} \right\} (J_\| R^2 C(2) \| J_\|)(J_f R^2 C(2) \| J_f). \quad (B-13)
\]

Since the phase of the 6-j is \((-1)^{J_\| + J_f + 1}\), it is easy to see that this is always positive.

Equations (B-11) to (B-14) can be identified with Eqs. (10) and (11) in the text.

The reduced matrix elements can be calculated in the usual way in terms of one-electron wave functions.
APPENDIX C: ANGULAR AVERAGE OVER PERTURBER ORBITS

According to Eqs. (3) and (9) the angular average for the $\langle F_{i j} \rangle$ term in Eq. (5) reduces to averaging

$$
\frac{2}{\Pi} \sum_{j=1}^{2} \left[ \frac{R \cdot r_j}{r_j^2} + \frac{3(R \cdot r_j)^2 - r_j^2 R^2}{2 r_j^2} \right] ; \quad r_j = \rho + v t_j
$$

(C-1)

over angles. The dipole (first)-quadrupole (second) cross terms give no contribution because of selection rules. In

$$
\langle i | R | i' \rangle \cdot \langle i' | R^2 | i \rangle = 0
$$

the first factor is zero if parity $i = \text{parity} (i')$; otherwise the second factor vanishes.

The two remaining terms are

$$
(R \cdot \rho)^2 + (R \cdot v)^2 t_1 t_2 + (R \cdot \rho)(R \cdot v)(t_1 + t_2)
$$

(C-2)

and

$$
\frac{1}{r_1 r_2} \left[ 9(R \cdot \rho + R \cdot v) t_1^2 (R \cdot \rho + R \cdot v) t_2^2 + R^4 (\rho^2 + v^2 t_1^2)^2 (\rho^2 + v^2 t_2^2)
\right.

\left. - 3 R^2 (\rho^2 + v^2 t_1^2) (R \cdot \rho + R \cdot v) t_2^2 - 3 R^2 (\rho^2 + v^2 t_2^2) (R \cdot \rho + R \cdot v) t_1^2 \right]
$$

(C-3)

for dipole and quadrupole, respectively.

Since $\{ \rho \} = 0$, $\{ \rho^2 \} = \frac{\rho^2}{3}$, $\{ \rho \, v \} = 0$,

(C-4)

the third term in Eq. (C-2) averages out, and the remaining ones, with

$$
\{ (R \cdot \rho)^2 \} = R \cdot R \frac{\rho^2}{3}
$$

and

$$
\{ (R \cdot v)^2 \} = R \cdot R \frac{v^2}{3}
$$

(C-5)

give

$$
\frac{1}{3} R \cdot R (\rho^2 + v^2 t_1 t_2)
$$

Thus, the dipole term gives, using the closure condition

$$
\langle F_{i j} \rangle = \frac{a^2}{3 \rho^2 v^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx_1 dx_2 \frac{iz(x_1 - x_2)}{(1 + x_1)^{3/2} (1 + x_2^{2/3})} |j \langle R | j' \rangle|^2
$$

(C-6)
with \( x_k = \frac{v_{tk}}{\rho} \), \( z = \frac{\omega_{1j}\rho}{v} \), i.e., the GBKO result, and the dipole portion of Eq. (18) [see Appendix A].

The factor \( a_0^2 \) serves to put the matrix elements in terms of the Bohr radius.

The quadrupole term (C-3) can be written as

\[
\frac{1}{r_1 r_2} \left[ \frac{1}{r_1^2 + r_2^2} \left( 9(R\cdot\rho)^4 + 9(R\cdot\rho)^2(R\cdot\nu)^2 + 9(R\cdot\nu)^4 \right) \right] \]

\[
-3r_1 r_2 \left( (r_1^2 + r_2^2) + (R\cdot\nu)^2 (r_1^2 + r_2^2) \right) \]

(C-7)

when Eqs. (C-4) are supplemented by \( \{\rho_{1j}^3\} = \{\rho_{1j}^3\} = 0 \).

The angular average \( \langle \rho_1 \rangle \) over terms involving \( \rho_1 \) or \( \nu_1 \) alone is easily carried out, e.g.,

\[
\{\rho_{1j}^4\} = \frac{1}{4\pi} \int d\Omega \rho_{1j}^4 \Omega = \frac{4}{5}
\]

as the average over solid angles \( \Omega \). For mixed terms one notes that \( \rho \cdot \nu = 0 \), so that \( \nu = (\hat{\phi} \sin \alpha + \hat{\theta} \cos \alpha)v \) in terms of the unit vectors \( \hat{\phi} \) and \( \hat{\theta} \) in the respective directions. The averages become

\[
\{\rho_{1j}^2\} = \frac{1}{8\pi} \int_0^{2\pi} d\alpha \int_0^\pi \rho_{1j}^2(\alpha) \Omega_1^2(\alpha) \Omega_2(\alpha,\alpha)
\]

\[
= \frac{\rho_{1j}^2 \nu_1^2}{15} \left( 2 - \delta_{ij} \right) \quad (C-8)
\]

From \( \rho \cdot \nu = 0 \) follows \( \frac{1}{2}\{\rho_{1j}^2\nu_{1j}\} = -\{\rho_{1j}^2\nu_{1j}\} \), etc. With, accordingly,

\[
\{\rho_{1j}^4\} = \rho_{1j}^4(R\cdot\rho)^2/5 \quad \text{and} \quad \{\rho_{1j}^2(R\cdot\nu)^2\} = \rho_{1j}^2(R\cdot\nu)^2/15
\]

the quadrupole term (C-7) now becomes

\[
\frac{2(R\cdot\nu)^2}{5r_1 r_2} \left[ 2r_1^2 r_2^2 - 3\rho^2 \nu^2 (t_1 - t_2)^2 \right] \quad \text{and}
\]
\[
\langle F_{j} \rangle = \frac{2}{5} \sum_{j} a_{j}^{4} \frac{e_{j}}{4 \sqrt{2}} \int_{-\infty}^{x_{1}} dx_{1} \int_{-\infty}^{x_{2}} dx_{2} \left\{ \frac{i z (x_{1} - x_{2})}{(1 + x_{1}^{2})^{5/2} (1 + x_{2}^{2})^{5/2}} \right\} \left[ \frac{2 (1 + x_{1}^{2}) (1 + x_{2}^{2}) - 3 (x_{1} - x_{2})^{2}}{(1 + x_{1}^{2})^{5/2} (1 + x_{2}^{2})^{5/2}} \right] |\langle j | R \cdot R | j' \rangle |^{2}.
\]

(C-9)

Comparison with Appendix A, where the functions \( A_{4} \) and \( B_{4} \) are defined, shows that Eq. (18) is now derived from Eqs. (3) and (5).

Naturally, the derivation is the same for initial \((j=i)\) and final \((j=f)\) level of the transition. The term \( \langle F_{if} \rangle \) is more conveniently handled by other means (Appendix B).
APPENDIX D: SYMMETRIZATION

We have seen that the real part of \( (1 - \langle i | S | i \rangle \langle f | S^{-1} | f \rangle)^{\text{Av}} \) can be put in terms of the probability of an inelastic transition between states \(|i\rangle\) and \(|i'\rangle\), i.e., \( P_{ii'} \). And hence the width can be put in terms of the cross section \( \sigma_{ij} \) such that

\[
\sigma_{ij} = \int_{0}^{\infty} P_{ij}(\rho_1) \ 2\pi \rho_1 d\rho_1.
\]

Symmetrization of the classical path results by a suitable average between initial and final velocities attempts to take into account both conservation of energy and conservation of angular momentum.\(^{21,24}\)

If during a collision the atom changes from \(|i\rangle\) to \(|j\rangle\) the angular momenta in the perturber motion are

\[
L_i = m v_i \rho_i \quad L_j = m v_j \rho_j
\]

with \( \Delta L = \pm 1 \) for dipole transition by conservation of angular momentum.

For large angular momenta it is usually a good approximation to take \( L_i = L_j = L \). Also, \( m v_i^2/2 - m v_j^2/2 = \frac{\hbar^2}{\lambda} \omega_{ji} \) (conservation of energy). Thus for \( v_i^2 \leq 2\hbar \omega_{ji}/m \), \( P_{ji} = 0 \) and the cross section is zero (i.e., below threshold).

If we consider the collision as a reversible classical process, we have the following reciprocity relation between the probability for a transition from \( i \) to \( j \) for an impact parameter \( \rho_i \) and that from \( j \) to \( i \) for an impact parameter \( \rho_j \), i.e., \( (2J_i + 1) P_{ij}(\rho_i) = (2J_j + 1) P_{ji}(\rho_j) \) or

\[
(2J_i + 1) P_{ij}(L) = (2J_j + 1) P_{ji}(L)
\]

where we have taken the statistical weights of the states into account. (A similar reciprocity condition holds for S-matrix elements.)
Now consider

\[ z_{ij} = \frac{\omega_{ij} \rho}{v} = \frac{\rho v \omega_{ij}}{v^2}. \]

Due to conservation of angular momentum \( \rho v \) is constant for a collision, so \( z \) can be symmetrized between the initial and final states by putting

\[ \tilde{z}_{ij} = \frac{\rho v \omega_{ij}}{(v_i^2 + v_f^2)/2} = \frac{\rho v \omega_{ij}}{v^2 - \kappa \omega_{ij}/m}. \]

Thus, symmetrization of real parts of \( \langle F_{ii} \rangle^{(2)} \) and \( \langle F_{ij} \rangle^{(4)} \) gives

\[ \text{Re}(\langle F_{ii} \rangle^{(2)} + \langle F_{ij} \rangle^{(4)})/\hat{m}^2 \]

\[ = \frac{2}{3} \left( \frac{\hbar}{m} \right)^2 \frac{1}{(\rho v)^2} \sum_{J_{i1}} \frac{(J_{i1} || \hat{R}^2 C(2)|| J_{i1})^2}{(2J_{i1} + 1)} A_2(\tilde{z}_{ii}) \]

\[ + \frac{a}{10} \left( \frac{\hbar}{m} \right)^2 \frac{(v^2 - \kappa \omega_{ii}/m)}{(\rho v)^4} \sum_{J_{i1}} \frac{(J_{i1} || \hat{R}^2 C(2)|| J_{i1})^2}{(2J_{i1} + 1)} A_4(\tilde{z}_{ii}), \]

where \( A(\tilde{z}_{ii}) = 0 \) for \( v^2 < 2\kappa \omega_{ii}/m \).

In symmetrizing \( \langle F_{ii} \rangle^{(4)} \) we have also had to symmetrize

\[ 1/\rho v^2 = v_i^2/(\rho v)^4 \rightarrow \frac{v_i^2 + v_f^2}{2(\rho v)^4} \]

since \( \rho v = L/m \) is invariant.

Similarly, integration with respect to \( \rho \) from some value \( \rho_{\text{min}} \) gives \( a_2(z) \) and \( a_4(z) \) terms which again can be symmetrized. Problems arise when the symmetrization is extended to arguments of the \( B \) functions which describe the shift. Since only elastic collisions can give rise to a shift, \( l \) and symmetrization only makes sense when \( v_i \neq v_j \) (but \( v_i = v_j \) for elastic events), the arguments \( z \) of the \( B \) functions should not be symmetrized. Only
unsymmetrized $B(z)$ will have the proper adiabatic limit of $B(z) \approx \pi/4z$ for $z \to \infty$ or $v \to 0$. Under the same circumstances a $B(\tilde{z})$ would have been equal to zero, if $v^2 < 2\hbar \omega_{ij}/m$ ($\omega_{ij} > 0$) (since by the dispersion relationship $B(\tilde{z}) = 2\tilde{z}/\pi P.V. \int_0^\infty A(\tilde{z}) d\tilde{z}'/(\tilde{z}^2 - \tilde{z}'^2)$, with $\tilde{z}$ being effectively a $\rho$ integration, we would have $B(\tilde{z}) = 0$ whenever $A(\tilde{z}) = 0$. It is precisely for $z \to \infty$ that the $B$ functions are important and they should reduce to the proper limit there. The loss of the dispersion relation between $B$ and $A$ for small $z$ is not disturbing or surprising, since strong collisions, which are not described by $A$ and $B$ obtained from the second order term in the Dyson expansion, become important in that range. The dispersion relation connects real and imaginary parts of the exact $S$-matrix, not necessarily the approximate one. In the high temperature limit $(z \to 0)$ where weak collisions dominate, the symmetrization is unimportant, and the dispersion relationship holds between the $A$ and $B$ function.

Notice that this symmetrization is not the only one, an alternative to $v^2 \to (v_i^2 + v_f^2)/2$ is $(v_i + v_f)^2/4$ (which can be found by comparison of the classical path and a WKB approximation for $P_{if}$).

Also, for this symmetrization procedure, the angular momentum $L = m v \rho$ has to be constant. This limits the validity to $\xi = L/\hbar \gg 1$, however, Baranger shows that this quantum number is large compared to one even for the closest collisions (small $\rho$) for which the classical path impact theory can be used. It is in fact a validity criterion for the classical path approximation.
REFERENCES


