Quantum theory of spectral-line shifts and broadening for hyperfine atomic transitions in a buffer gas medium

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The problem of the shape of spectral lines due to hyperfine transitions in active atoms in an inert buffer gas atmosphere is solved. The solution is based on the quantum-mechanical kinetic equation for the density matrix of the radiating atom. The derivation and solution of this equation is based on the following assumptions: the collision time is small in comparison with the mean free time, the probability of reorientation of electron and nuclear spins is small in each collision, and the number of collisions during the emission time is large. It is shown that the line width and shape depend significantly on the strength of the weak magnetic field producing Zeeman splitting of the hyperfine structure levels. In zero magnetic field, the line width is comparable with the line shift. As the field increases to a value in the range 0.01–1 Oe, the width is found to decrease appreciably and becomes smaller than the shift by a few orders of magnitude. The line shape is then approximately Lorentzian. The shifts and widths due to the combined operation of the Doppler effect and collisions are expressed in terms of exact quantum-mechanical scattering amplitudes. Quasiclassical expressions are obtained for these quantities together with quantum corrections due to the nonclassical character of the translational motion of the atoms. For light atoms, these corrections can amount to up to 10%.

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1. INTRODUCTION

Detailed knowledge of the shape of spectral lines, especially those associated with hyperfine transitions, is important for many applications, for example, radio astronomy, resonance experiments in optics, quantum frequency standards, and so on. The shift of spectral lines due to hyperfine transitions, which is produced by collisions between radiating atoms in an inert buffer gas, has been calculated by a number of authors,[1–8] but all these calculations were performed for the two-level system in the quasiclassical approximation to the motion of the colliding atoms. However, real atoms have more than two levels and the quasiclassical approximation is not really valid for light atoms. In fact, quantum-mechanical corrections may well be important. Line broadening was not calculated in most of these papers although the line width is important for many purposes, for example, when the atomic system is exposed to resonant radio or optical frequency pump fields. This problem was partially solved in our previous paper,[7,8] but a general enough quantum-mechanical theory of broadening of hyperfine structure lines with allowance for many sublevels has not been available. Published calculations have frequently been based on special models (see, for example, Rautian and Sobel'man[9] and Sobel'man[10]), so that it has been difficult to estimate the accuracy of the results obtained in this way.

For the reasons indicated above, there is considerable interest in a rigorous quantum-mechanical solution of the problem of the line shape, capable of yielding a result with a controllable degree of precision. In this paper, we use the quantum-mechanical kinetic equation to calculate the correlation function in terms of which the line shape is expressed. The interaction between the atoms is taken into account in this equation in terms of the exact scattering amplitudes which are different for different hyperfine structure sublevels. To obtain an approximate solution of the kinetic equation, we assume that the mean free time of the radiating atom is small in comparison with the characteristic time of the problem, i.e., the emission time, and we carry out an expansion in terms of the reciprocal powers of the collision frequency, which is analogous to the well-known Enskog-Chapman expansion.

It turns out that the width and shape of a line depend significantly on the magnitude of the weak magnetic field producing Zeeman splitting of the hyperfine structure levels. In zero magnetic field, the line width is comparable with the line shift. As the field increases up to a value in the range 0.01–1 Oe, which depends on the scattering amplitudes and the collision frequency, the width is found to decrease substantially and becomes smaller than the shift by a few orders of magnitude. The line shape is then nearly Lorentzian.

The shift Δ and the width Γ will be expressed in terms of the exact scattering amplitude of the atoms. They will then be expanded in terms of the quasiclassical parameter. Numerical results will be obtained for a number of pairs of active and buffer atoms. Both general formulas and particular numerical data show that the Foley relation[11] (see also Sobel'man[10]), namely, $\Gamma/|\Delta| \sim 1$, which is valid to within an order of magnitude in the optical band, is not valid in the present case.

We note that the quantum-mechanical kinetic equation was used previously for optical transitions in gases by Pestov and Rautian[12] and by Alekseev *et al.*[13] In the former paper, the shape of the spectral lines was not analyzed in detail. The results of the latter paper cannot be directly applied to hyperfine structure transitions which, as already mentioned, have specific properties related to the strong dependence of the width on the magnetic field, and the relationship between the shift and the width.

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2. THE KINETIC EQUATION

The probability of emission of a photon by a radiating ("active") atom, averaged over all its initial excited states μ_0 and summed over the final states ν_0, is given by

$$dW_{\varkappa\sigma}=\frac{2}{\hbar}\operatorname{Re}\sum_{\substack{\mu_0\nu_0\\ \mu\nu}} w_{\mu_0}F_{\mu\nu}(-\varkappa,\sigma)F_{\mu_0\nu_0}(\varkappa,\sigma)$$
$$\times\int\frac{d^3k}{(2\pi)^3}f_0^a(k)\int\frac{d^3p}{(2\pi)^3}f_{\mu_0\nu_0,\mu\nu}(\mathbf{k},\mathbf{p};\varkappa;\omega_\varkappa)\frac{d^3\varkappa}{(2\pi)^3}, \tag{1}$$

where $\varkappa$, σ, and $\omega_\varkappa$ are, respectively, the wave vector, polarization, and frequency of the emitted photon, $\mathbf{k}$ and $\mathbf{p}$ are the initial and final wave vectors of the active atom μ_0, ν_0, and μ, ν are its internal states, $f_0^a(k)w_{\mu_0}$ is the initial diagonal density matrix of the excited atom, and $F_{\mu\nu}$ are the matrix elements of the electromagnetic interaction. The quantities $f_{\mu_0\nu_0,\mu\nu}(\mathbf{k},\mathbf{p};\varkappa;\omega_\varkappa)$ are the Fourier transforms of the nondiagonal elements of the two-particle density matrix of the active atoms. Since there may be many collisions between the active atoms and the buffer atoms during the emission time, these Fourier transforms must be determined by deriving and solving the appropriate kinetic equation. The derivation of this equation is not in itself trivial because the quantities in which we are interested do not have classical analogs, and the equation for them cannot be obtained from simple balance considerations. The most satisfactory way of deriving the required equation is, in our view, the diagram method in the form put forward by Konstantinov and Perel'[14] (see also D'yakonov and Perel'[15]). It has the advantage, in comparison with the other possible approaches (see, for example, Alekseev *et al.*[13]), that it provides an indication of the accuracy of the approximations employed at all stages of the calculation, and can be generalized to more complicated cases, for example, when the active atoms are exposed to radio-frequency and optical pump fields.[16] Within the framework of this method, one can conveniently carry out a systematic allowance for the influence of collisions in radiative processes and in other situations (an example can be found in Toptygin[17]). However, because of lack of space, we cannot reproduce the derivation here and quote only the final result.

The kinetic equation for the density matrix of a radiating atom can be written in the form

$$\frac{\partial f_{\mu\nu}(\mathbf{k},\mathbf{p};\varkappa;t)}{\partial t}+i\Big\{\omega_{\mu\nu}-\frac{2\pi\hbar}{m}\int\frac{d^3q}{(2\pi)^3}N_q^b\operatorname{Re}\left[a_{\mu\mu}(p_0,p_0)-a_{\nu\nu}(p_0,p_0)\right]$$
$$+\varkappa\mathbf{v}\Big\}f_{\mu\nu}(\mathbf{k},\mathbf{p};\varkappa;t)=\delta_{\mathbf{kp}}\delta_{\mu_0\mu}\delta_{\nu_0\nu}\delta(t)-\frac{\hbar^3}{2m^2}\int\frac{d^3q}{(2\pi)^3}N_q^b$$
$$\times\int d^3p_0'\Big\{\sum_{\mu'}|a_{\mu\mu'}(\mathbf{p}_0,\mathbf{p}_0')|^2\delta(E_0+\varepsilon_\mu-E_0'-\varepsilon_{\mu'})$$
$$+\sum_{\nu'}|a_{\nu\nu'}(\mathbf{p}_0,\mathbf{p}_0')|^2\delta(E_0+\varepsilon_\nu-E_0'-\varepsilon_{\nu'})f_{\mu\nu}(\mathbf{k},\mathbf{p};\varkappa;t)\Big\}$$
$$+\frac{\hbar^3}{m^2}\sum_{\mu'\nu'}\int\frac{d^3q'}{(2\pi)^3}N_{q'}^b\int d^3p'a_{\mu'\mu}(\mathbf{p}_0',\mathbf{p}_0)a_{\nu'\nu}^*(\mathbf{p}_0',\mathbf{p}_0)$$
$$\times f_{\mu'\nu'}(\mathbf{k},\mathbf{p}';\varkappa;t)\delta(E_0+\varepsilon_\mu-E_0'-\varepsilon_{\mu'}), \tag{2}$$

where $\omega_{\mu\nu}=(\varepsilon_\mu-\varepsilon_\nu)/\hbar$ is the transition frequency, ε_μ, ε_ν are the internal energies of the active atom, $E_0=\hbar^2p_0^2/(2m)$ is the energy of relative motion of the active and buffer gas atoms, m is their reduced mass,

$$\mathbf{p}_0=\mu_b\mathbf{p}-\mu_a\mathbf{q},\quad \mathbf{p}_0'=\mu_b\mathbf{p}'-\mu_a\mathbf{q}' \tag{3}$$

are the wave vectors of relative motion of the atoms before and after the collision,

$$\mu_a=m_a/(m_a+m_b),\quad \mu_b=m_b/(m_a+m_b), \tag{4}$$

m_a and m_b are the masses of the active and buffer gas atoms, and $\mathbf{p},\mathbf{q}$ and $\mathbf{p}',\mathbf{q}'$ are their wave vectors in the laboratory frame before and after collision. The quantities $a_{\mu\mu'}(p_0,p_0')$ are the scattering amplitudes of the active atom between the state $\mathbf{p}_0$, μ and p_0', μ' due to a collision with a buffer gas atom or molecule. The lengths of the vectors $\mathbf{p}_0,\mathbf{p}_0'$ are related by the energy conservation law:

$$E_0+\varepsilon_\mu=E_0'+\varepsilon_{\mu'}. \tag{5}$$

The quantity $N_q^b=N_bf_0^b(q)$ represents the occupation numbers of the buffer atoms, N_b is their concentration, and $f_0^b(q)$ is the equilibrium distribution function. The initial-state subscripts μ_0, ν_0, are omitted from $f_{\mu\nu}$. The last term in (2) can be interpreted as the "input" term of the kinetic equation ("input" into the states μ and ν). The remaining integral terms are "output" terms; the term $\varkappa\cdot\mathbf{v}$ takes into account the Doppler frequency shift due to the thermal motion of the active atom.

The derivation of (2) was based on the following approximations: a) the collisions were assumed to be binary and instantaneous; b) collisions between active atoms were neglected; c) the line shift and width, and the frequency detuning, were assumed small in comparison with the frequency of the radiated line (this ensures that, the last sum over μ', ν' contains only terms in which $\varepsilon_\mu-\varepsilon_\nu=\varepsilon_{\mu'}-\varepsilon_{\nu'}$ to within $\hbar|\Delta\omega+i\Gamma/2|$, and which correspond to the superposition of the spectral lines), and d) the radiative widths and shifts γ_r and Δ_r of the levels are not taken into account, nor are terms $\Delta'-i\gamma'/2$ that are linear in the forward-scattering amplitudes and correspond to transitions to states $\mu'\neq\mu$ and $\nu'\neq\nu$ for $\varepsilon_\mu=\varepsilon_{\mu'}$ and $\varepsilon_\nu=\varepsilon_{\nu'}$ (this is connected with the fact that we are considering hyperfine structure transitions in the presence of Zeeman splitting when Δ' and γ' vanish and Δ_r and γ_r are very small).

It is important to note that Eq. (2), which is the starting point for our analysis, is similar to Eq. (13) of Alekseev *et al.*[13] The latter equation suffers from a mistake in the argument of the δ-function but, when this is removed and the same notation is employed as in the present paper, the differences between the two equations are connected only with the particular properties of the hyperfine structure transitions considered here (transition energy and momentum of the radiofrequency photon both small).

3. CALCULATION OF THE SHIFT AND WIDTH OF A SPECTRAL LINE

We must now identify the small parameters in terms of which we can expand the solutions of (2). One of them

TABLE I. Shifts, broadening, and auxiliary parameters.

Pair A—B	T, K	Experiment: Δ/p, Hz/Torr	Experiment: Γ^{na}, Hz/Torr	Experiment: Γ^{a}, Hz/Torr	Experiment: σ^{na}, 10^{-25} cm² [18]	Theory: Δ/p, Hz/Torr	Theory: Γ^{na}, Hz/Torr	Theory: Γ^{a}, H_3/Torr, [equation(50)]	Theory: σ^{na}, 10^{-25} cm²	ν, 10^6 sec	$\eta \sim \frac{\lvert\Delta\rvert}{\nu}$	$\eta \sim \frac{\Gamma^a}{\lvert\Delta\rvert}$
H–He	173	6.52	–	–	–	6.48 [6]	–	–	–	·	–	–
	323	5.40±0.27	–	–		5.36 [6]	–	$2.5\cdot10^{-4}$ *	–	7	10^{-5}	10^{-5}
	673	4.42	–	–	–	4.18 [6]	–	$3\cdot10^{-5}$	–	–	–	–
Na^{23}–He	295	130 [18]	$8.4\cdot10^{-5}$	–	0.22	128 [3]	–	$4.7\cdot10^{-2}$ *	–	11.6	10^{-5}	10^{-4}
Rb^{87}–He	303	720 [18]	$1.20\cdot10^{-3}$	–	3.3	510 **	–	0.3	–	157	10^{-5}	10^{-4}
Rb^{87}–Ar	303	−60 [28]	0.15	$<10^{-2}$	1100	−160 **	0.25	$4\cdot10^{-3}$	1900 [23]	84	10^{-6}	10^{-4}
Rb^{87}–Kr	303	−559 [28]	25	–	$2.3\cdot10^5$	−648 **	5.0	0.4	$0.48\cdot10^5$ [7]	68	10^{-5}	10^{-4}
Rb^{87}–N_2	303	508 [28]	0.12	–	570	–	–	0.1	–	116	10^{-4}	10^{-4}
Cs^{133}–He	303	1200 [18]	0.10	–	280	1065 **	–	0.7	–	173	10^{-5}	10^{-5}
Cs^{133}–Ar	303	−212 [18]	12	<0.5	$9.7\cdot10^3$ [29]	−226 **	—	0.04	–	86	10^{-5}	10^{-4}
Cs^{133}–Xe	303	−2350 [18]	110	–	$1.2\cdot10^5$ [29]	−1680 **	—	7	–	74	10^{-4}	10^{-3}

*Calculations performed in our previous paper[7,8] using $\Delta\omega(R)$ from the paper by Ray *et al.*[3]
**Calculations carried out by M. B. Gornyi (preliminary results).

is the small addition to the elastic scattering amplitude of the atoms due to the hyperfine interaction:

$$a_{\mu\mu}(\mathbf{p}_0', \mathbf{p}_0) = a(\mathbf{p}_0', \mathbf{p}_0) + \alpha_{\mu\mu}(\mathbf{p}_0', \mathbf{p}_0), \tag{6}$$

where $a(\mathbf{p}_0', \mathbf{p}_0) = a(p_0, \theta_0)$ is the amplitude when the hyperfine interaction is ignored (the gas-kinetic amplitude). The order of magnitude result is $\eta \sim |\alpha_{\mu\mu}/a| \sim |U_{hs}/U| \ll 1$, where U_{hs} is the energy of the hyperfine structure interaction and U is the total effective energy associated with the interaction between the atoms (of the order of their thermal energy). A more accurate numerical estimate will show that η varies from $\eta \sim 10^{-5}$ for the light pair of atoms H–He up to $\eta \sim 0.01$ for the heavy pair Cs–Xe. The transition amplitude between the hyperfine-structure and Zeeman levels $a_{\alpha\alpha'} = \alpha_{\mu\mu'}$ for $\mu' \neq \mu$ is frequently not greater in order of magnitude than $\alpha_{\mu\mu}$. This follows from experimental data[18–22] and theoretical estimates[7,8,23,24] (the transition cross section is $|\alpha_{\mu\mu'}|^2 \sim 10^{-19}$–$10^{-26}$ cm², so that $|\alpha_{\mu\mu'}/a| \sim 10^{-2}$–$10^{-5}$). The transition amplitude for the interaction between alkali atoms and N_2, H_2, D_2, CH_4, C_2H_6, C_2H_4, cyclohexane, and other molecules is of roughly the same order of magnitude.[18] For the transition amplitudes between hyperfine structure levels of the alkali-like ions Sr^+, Ba^+, it is found that $|\alpha_{\mu\mu'}/a| \lesssim 10^{-2}$–$5\times10^{-2}$.[18]

The small transition amplitudes are also characteristic for atoms with total electron angular momentum $J = 1/2$. This is connected with the selection rule $M_J \nrightarrow -M_J$[24] for transitions between all the sublevels of a given multiplet, and has been confirmed experimentally[22] for the thallium atom in the $^2P_{1/2}$ ground state (transition cross section between 10^{-19} and 10^{-17} cm², so that $|\alpha_{\mu\mu'}/a| \lesssim 10^{-2}$–$10^{-1}$). Although the amplitudes $\alpha_{\mu\mu}$ and $\alpha_{\mu\mu'}$ ($\mu' \neq \mu$) may differ in magnitude, we shall characterize them both by the single parameter η, assuming that $\alpha_{\mu\mu}$, $\alpha_{\mu\mu'} \sim \eta a$, where $\eta \ll 1$. This will be done for order of magnitude purposes.

There is one other small parameter, namely, the ratio of the mean free path for elastic scattering $L \approx 1/(N_b \sigma)$ and the wavelength λ of the radiated photon. At pressures of a few torr ($N_b \sim 10^{17}$ cm^{-3}), this ratio is $L/\lambda \sim 10^{-2}$–10^{-3} for hyperfine structure transitions. The collision frequency between active and buffer gas atoms, $\nu = \bar{v}/L \sim 10^7$ sec^{-1}, will be assumed to be large in comparison with the total line width Γ, its shift Δ, and the frequency detuning (see Table I).

We shall also assume that the degenerate hyperfine structure levels are split by a constant magnetic field H_0 into Zeeman sublevels. The separation between these sublevels, and also between the spectral components, will be assumed to be arbitrary for the time being. The presence of a magnetic field is usually the rule rather than the exception: it is either the stabilizing field in microwave devices or the geomagnetic (stellar magnetic) field in astrophysical applications.

Let us now multiply both sides of (2) by the initial distribution function $f_0^a(k)$ of the excited atom, which we shall assume to be the equilibrium function, and sum over k. Each suffix μ and ν represents a set of two quantum numbers, namely, F and M. Henceforth, we shall indicate only the magnetic quantum numbers M_1 and M_2. The suffix 1 will refer to the lower and the suffix 2 to the upper hyperfine structure level. We shall also take the Fourier transform of (2) with respect to time, and substitute into it the expansion (6) for the scattering amplitudes. The final result is the set of equations

$$\begin{aligned} &i\left(\omega_{M_2M_1} - \omega + \varkappa v + \hat{\Delta}_{M_2M_1} - \frac{i}{2}\hat{\Gamma}_{M_2M_1}\right) f_{M_2M_1}(\mathbf{p}; \varkappa; \omega) \\ &+ \sum_{M_2'M_1'}{}' \left(i\hat{\Delta}_{M_2M_1}^{M_2'M_1'} + \frac{1}{2}\hat{\Gamma}_{M_2M_1}^{M_2'M_1'}\right) f_{M_2'M_1'}(\mathbf{p}; \varkappa; \omega) \\ &= \frac{1}{2\pi} f_0^a(p)\delta_{M_2M_2'}\delta_{M_1M_1'}\sigma + \hat{S} f_{M_2M_1}(\mathbf{p}; \varkappa; \omega). \end{aligned} \tag{7}$$

The sum over M_1' and M_2' involves only the nondiagonal terms, i.e., either $M_1' \neq M_1$ or $M_2' \neq M_2$.

The operator $\hat{S}$ describes collisions between active and buffer-gas atoms without taking into account the hyperfine interaction, and is the usual Boltzmann collision operator; $\hat{\Delta}$ and $\hat{\Gamma}$ are the shift and broadening operators. All the operators are integral:

$$\hat{S} f_{M_2M_1}(\mathbf{p}; \varkappa, \omega) = \int S(\mathbf{p}, \mathbf{p}') f_{M_2M_1}(\mathbf{p}', \varkappa, \omega)\, d^3p' \tag{8}$$

and so on. The kernel of $\hat{S}$ is

$$\begin{aligned} S(\mathbf{p}, \mathbf{p}') &= -\int \frac{d^3q}{(2\pi)^3} N_q{}^b v_0 \sigma(p_0)\delta(\mathbf{p}-\mathbf{p}') \\ &+ \frac{\hbar^2}{m^2}\int \frac{d^3q'}{(2\pi)^3} N_{q'}{}^b |a(\mathbf{p}_0', \mathbf{p}_0)|^2 \delta(E_0 - E_0'), \end{aligned} \tag{9}$$

where $\sigma(p_0)=\int|a(p_0,\theta_0)|^2d\Omega_0$ is the total collision cross section of the atoms. The kernels of the remaining operators are given by the following expressions:

$$\Delta_{M_2M_1}(\mathbf{p},\mathbf{p}')=-\frac{2\pi\hbar}{m}\int\frac{d^3q}{(2\pi)^3}N_q{}^b\,\mathrm{Re}[\alpha_{M_2M_2}(\mathbf{p}_0,\mathbf{p}_0)-\alpha_{M_1M_1}(\mathbf{p}_0,\mathbf{p}_0)]\delta(\mathbf{p}-\mathbf{p}')+\frac{\hbar^2}{m^2}\int\frac{d^3q'}{(2\pi)^3}N_{q'}{}^b\times\mathrm{Im}\{a^*(\mathbf{p}_0',\mathbf{p}_0)[\alpha_{M_1M_1}(\mathbf{p}_0',\mathbf{p}_0)-\alpha_{M_2M_2}(\mathbf{p}_0',\mathbf{p}_0)]+\alpha_{M_1M_1}(\mathbf{p}_0',\mathbf{p}_0)\alpha^*_{M_2M_2}(\mathbf{p}_0',\mathbf{p}_0)\}\delta(E_0-E_0'),\tag{10}$$

$$-\frac{1}{2}\Gamma_{M_2M_1}(\mathbf{p},\mathbf{p}')=-\frac{\hbar^2}{2m^2}\int\frac{d^3q}{(2\pi)^3}N_q{}^b\cdot\times\int d^3\tilde{p}_0\{2\,\mathrm{Re}\,a^*(\mathbf{p}_0,\tilde{\mathbf{p}}_0)[\alpha_{M_2M_2}(\mathbf{p}_0,\tilde{\mathbf{p}}_0)+\alpha_{M_1M_1}(\mathbf{p}_0,\tilde{\mathbf{p}}_0)]+\sum_M(|\alpha_{M_2M}(\mathbf{p}_0,\tilde{\mathbf{p}}_0)|^2+|\alpha_{M_1M}(\mathbf{p}_0,\tilde{\mathbf{p}}_0)|^2)\}\delta(E_0-\tilde{E}_0)\delta(\mathbf{p}-\mathbf{p}')+\frac{\hbar^2}{m^2}\int\frac{d^3q'}{(2\pi)^3}N_{q'}{}^b\,\mathrm{Re}\{a^*(\mathbf{p}_0',\mathbf{p}_0)[\alpha_{M_2M_2}(\mathbf{p}_0',\mathbf{p}_0)+\alpha_{M_1M_1}(\mathbf{p}_0',\mathbf{p}_0)]+\alpha_{M_1M_1}(\mathbf{p}_0',\mathbf{p}_0)\alpha^*_{M_2M_2}(\mathbf{p}_0',\mathbf{p}_0)\}\delta(E_0-E_0'),\tag{11}$$

$$i\Delta_{M_2M_1}^{M_2'M_1'}(\mathbf{p}',\mathbf{p})+\frac{1}{2}\Gamma_{M_2M_1}^{M_2'M_1'}(\mathbf{p}',\mathbf{p})=\frac{\hbar^2}{m^2}\int\frac{d^3q'}{(2\pi)^3}N_{q'}{}^b\times\{a^*(\mathbf{p}_0',\mathbf{p}_0)\alpha_{M_1'M_1}(\mathbf{p}_0',\mathbf{p}_0)\delta_{M_2'M_2}+a(\mathbf{p}_0',\mathbf{p}_0)\alpha^*_{M_2'M_1'}(\mathbf{p}_0',\mathbf{p}_0)\delta_{M_1'M_1}+\alpha_{M_1'M_1}(\mathbf{p}_0',\mathbf{p}_0)\alpha^*_{M_2'M_2}(\mathbf{p}_0',\mathbf{p}_0)\}\delta(E_0-E_0'+\varepsilon_{M_2}-\varepsilon_{M_2'}).\tag{12}$$

The collision operator $\hat{S}$ on the right-hand side of (7) is of the order of $\nu\sim N_b v_0 a^2$, whereas the broadening and shift operators, $\hat{\Gamma}$ and $\hat{\Delta}$, on the left-hand side of (7), do not exceed $N_b v_0 a\alpha\sim\eta\nu$ in order of magnitude. This means that the Maxwell distribution is formed for the resulting atom in a time that is small in comparison with the other characteristic times of the problem, so that the difference between the matrix elements $f_{M_2M_1}(\mathbf{p};\varkappa;\omega)$ and the Maxwell function $f_0^a(p)$ is small:

$$f_{M_2M_1}(\mathbf{p},\varkappa,\omega)=f_0^a(p)[1+G_{M_2M_1}(\mathbf{p})]\varphi_{M_2M_1}(\omega),\tag{13}$$

where $|G_{M_1M_2}(\mathbf{p})|$ is of the order of η or L/λ and the coefficients $\varphi_{M_2M_1}(\lambda)$ are independent of $\mathbf{p}$. In the zero-order approximation in η, L/λ, the equations in (7) are found to split, and the matrix elements $f^{(0)}_{M_2M_1}(\mathbf{p},\varkappa,\omega)$ satisfy independently the Boltzmann kinetic equation

$$\hat{S}f^{(0)}_{M_2M_1}(\mathbf{p},\varkappa,\omega)=0.\tag{14}$$

The small corrections $G_{M_2M_1}(\mathbf{p})$ will be sought in the form of an expansion in reciprocal powers of the collision frequency.

Let us substitute (13) in (7) and integrate with respect to $d^3p(2\pi)^3$. Since terms involving the collision operator $\hat{S}$ are found to vanish as a result of this procedure, the final expression is

$$i\varphi_{M_2M_1}(\omega)\left\{-\omega'_{M_2M_1}(1+\langle G_{M_2M_1}\rangle)+\langle\Delta_{M_2M_1}\rangle-\frac{i}{2}\langle\Gamma_{M_2M_1}\rangle+\langle(\varkappa\mathbf{v})G_{M_2M_1}(p)\rangle+\int\left(\hat{\Delta}_{M_2M_1}-\frac{i}{2}\hat{\Gamma}_{M_2M_1}\right)G_{M_2M_1}(\mathbf{p})f_0^a(p)\frac{d^3p}{(2\pi)^3}\right\}+\sum_{M_2'M_1'}{}'\left\{\langle D_{M_2M_1}^{M_2'M_1'}\rangle+\left\langle\left[i\hat{\Delta}_{M_2M_1}^{M_2'M_1'}+\frac{1}{2}\hat{\Gamma}_{M_2M_1}^{M_2'M_1'}\right]G_{M_2'M_1'}(\mathbf{p})\right\rangle\right\}\varphi_{M_2'M_1'}(\omega)=\frac{1}{2\pi}\delta_{M_2M_2'}\delta_{M_1M_1'},\tag{15}$$

where $\omega'_{M_2M_1}=\omega-\omega_{M_2M_1}$, $\langle\cdots\rangle$ represents averaging over the Maxwell distribution:

$$\langle G_{M_2M_1}\rangle=\int G_{M_2M_1}(p)f_0^a(p)\frac{d^3p}{(2\pi)^3}$$

and so on. The parameters $\langle\Delta_{M_2M_1}\rangle$, $\langle\Gamma_{M_2M_1}\rangle$ and the nondiagonal coefficients $\langle D_{M_2M_1}^{M_2'M_1'}\rangle$ are given by formulas that follow from (10)–(12):

$$\langle\Delta_{M_2M_1}\rangle=\langle\Delta_{M_2M_1}(p)\rangle,\tag{16}$$

$$\Delta_{M_2M_1}(p)=-\frac{2\pi\hbar}{m}\int\frac{d^3q}{(2\pi)^3}N_q{}^b\,\mathrm{Re}[\alpha_{M_2M_2}(p_0,0)-\alpha_{M_1M_1}(p_0,0)]+\int\frac{d^3q}{(2\pi)^3}N_q{}^bv_0\,\mathrm{Im}\int d\Omega_0a^*(p_0,\theta_0)[\alpha_{M_1M_1}(p_0,\theta_0)-\alpha_{M_2M_2}(p_0,\theta_0)],\theta_0=\sphericalangle(\mathbf{p}_0,\mathbf{p}_0').\tag{17}$$

$$\langle\Gamma_{M_2M_1}\rangle=\langle\Gamma^a_{M_2M_1}(p)\rangle+\langle\Gamma^{na}_{M_2M_1}(p)\rangle,\tag{18}$$

$$\Gamma^a_{M_2M_1}(p)=\int\frac{d^3q}{(2\pi)^3}N_q{}^bv_0\int|\alpha_{M_1M_1}(p_0,\theta_0)-\alpha_{M_2M_2}(p_0,\theta_0)|^2\,d\Omega_0,\tag{19}$$

$$\Gamma^{na}_{M_2M_1}(p)=\int\frac{d^3q}{(2\pi)^3}N_q{}^bv_0\sum_M{}'\int[|\alpha_{M_2M}(p_0,\theta_0)|^2+|\alpha_{M_1M}(p_0,\theta_0)|^2]d\Omega_0,\tag{20}$$

$$\langle D_{M_2M_1}^{M_2'M_1'}\rangle=i\langle\Delta_{M_2M_1}^{M_2'M_1'}(p)\rangle+\frac{1}{2}\langle\Gamma_{M_2M_1}^{M_2'M_1'}(p)\rangle,\tag{21}$$

$$i\Delta_{M_2M_1}^{M_2'M_1'}(p)+\frac{1}{2}\Gamma_{M_2M_1}^{M_2'M_1'}(p)=-N_b\int\frac{d^3q}{(2\pi)^3}N_q{}^bv_0\{a^*(p_0',p_0)\alpha_{M_1'M_1}(p_0',p_0)\delta_{M_2'M_2}+a(p_0',p_0)\alpha^*_{M_2'M_2}(p_0',p_0)\delta_{M_1'M_1}+\alpha^*_{M_2'M_2}(p_0',p_0)\alpha_{M_1'M_1}(p_0',p_0)\},\tag{22}$$

where $\langle\Gamma^a_{M_2M_1}\rangle$ is the adiabatic (transverse) broadening, connected with the adiabatic excitations of the active atom, and $\langle\Gamma^{na}_{M_2M_1}\rangle$ is the nonadiabatic (longitudinal) broadening, connected with transitions to other states. The explicit form of the operators $\hat{\Delta}^{M_2'M_1'}_{M_2M_1}$ and $\hat{\Gamma}^{M_2'M_1'}_{M_2M_1}$ follows from (12) and is not introduced here because terms containing these operators are smaller than $\langle\Delta^{M_2'M_1'}_{M_2M_1}\rangle$, $\langle\Gamma^{M_2'M_1'}_{M_2M_1}\rangle$ by a factor of η (in order of magnitude).

If the correction functions $G_{M_2M_1}$ have been determined (the evaluation of these functions will be considered below), we can use the set of algebraic equations given by (15) to calculate the quantities $\varphi_{M_2M_1}(\omega)$, in terms of which the spectral line shape is expressed [see (13) and (1)]. For arbitrary Zeeman splitting of the hyperfine structure levels, and if their number is large, the line shape is described by complicated expressions although there are no fundamental difficulties in calculating the line shape. Because of lack of space, we shall not reproduce these formulas here, but they do show that, for fields $H_0\ll\hbar\nu\eta/\mu_B\approx\eta$ [Oe] (when $\nu\approx10^7$ sec^{-1}), the line shift and broadening are both of the order of $\eta\nu$.

As the field is increased until $H_0>\hbar\nu\eta/\mu_B$, there is a significant splitting of the sublevels, and the spectral lines become narrower. Their shape in such fields depends on whether there is a superposition of the spectral components ($J=1/2$)

$$\omega_{M_2M_1}=\omega_0+\frac{M_1+M_2}{I+1/2}\frac{\mu_BH_0}{\hbar}+\left[2-\frac{M_1^2+M_2^2}{(I+1/2)^2}\right]\left(\frac{\mu_BH_0}{\hbar\omega_0}\right)^2\omega_0,\tag{23}$$

for the particular transition. If there is no superposition, and this is so in, for example, hydrogen ($F_1=0$, $F_2=1$), then for $H_0\gg\hbar\nu/\mu_B$ the set of equations given by (15) separates completely and only one equation is sufficient for evaluating the shape of an individual spectral line. For the frequently used transitions between the

sublevels $M_2=0$ and $M_1=0$, one can use the symmetry of the system with respect to this transition to take out one equation form (15) even for lower fields $H_0 \gg \hbar\nu\sqrt{\eta}/\mu_B$. In such cases, the spectral line shape is given by

$$I_{M_2M_1}(\omega)=\mathrm{Re}\int f_{M_2M_1}(p;\varkappa;\omega)\frac{d^3p}{(2\pi)^3}=\frac{1}{2\pi}\mathrm{Re}\left(\frac{i}{\Omega_{M_2M_1}}\right), \tag{24}$$

$$\Omega_{M_2M_1}=-\omega'_{M_2M_1}+\langle\Delta_{M_2M_1}\rangle-\frac{i}{2}\langle\Gamma_{M_2M_1}\rangle+\langle(\varkappa v)G_{M_2M_1}(p)\rangle$$
$$+i\,\mathrm{Im}\langle[\Delta_{M_2M_1}(p)-\langle\Delta_{M_2M_1}\rangle]G_{M_2M_1}(p)\rangle. \tag{25}$$

It is clear from (24) that the line shape is Lorentzian and that the shift $\langle\Delta_{M_2M_1}\rangle\sim\eta\nu$ is large in absolute magnitude in comparison with the collisional broadening

$$\Gamma^c_{M_2M_1}=\langle\Gamma_{M_2M_1}\rangle+2\,\mathrm{Re}\,i\langle[\Delta_{M_2M_1}(p)-\langle\Delta_{M_2M_1}\rangle]G_{M_2M_1}(p)\rangle\sim\eta^2\nu, \tag{26}$$

and the Doppler broadening

$$\Gamma^D_{M_2M_1}=2i\langle(\varkappa v)G_{M_2M_1}(p)\rangle\sim(L/\lambda)^2\nu. \tag{27}$$

We have omitted from (25) all terms in the shift of order higher than the first order in η. In (26) and (27), on the other hand, we have to retain all terms of order η^2 and $(L/\lambda)^2$.

In general, spectral lines can overlap, and (15) will contain a number of equations. For example, if the active atom is Rb^{87} in the ground state ($F_1=1$, $F_2=2$), then, for the transitions between the $M_2=0$ and $M_1=0$ states, we have the superposition of the following three lines if we neglect the term in (23) that is quadratic in H_0: $M_1=M_2=0$, $M_1=-M_2=1$, $M_1=-M_2=-1$. The set of equations in (15) for $H_0\gg\hbar\nu\sqrt{\eta}/\mu_B$ will then consist of only three equations. They lead to the following line shape:

$$I_{00}(\omega)=\frac{1}{2\pi}\mathrm{Re}\,i\left\{\Omega_{00}+\frac{\langle D_{00}^{1-1}\rangle\langle D_{1-1}^{00}\rangle}{\Omega_{1-1}}+\frac{\langle D_{00}^{-11}\rangle\langle D_{-11}^{00}\rangle}{\Omega_{-11}}\right\}^{-1}. \tag{28}$$

It is clear that this line shape is nearly Lorentzian, and the shift $\langle\Delta_{00}\rangle\sim\eta\nu$ is large in comparison with the line width, as in the preceding case. The fractional terms in the braces in (28) become negligible when $\nu/\omega_0\gg\eta$ or $H_0\gg\hbar(\nu\omega_0\eta)^{1/2}/\mu_B$. In either case, they can be neglected so that (28) becomes identical with (24).

We shall seek the correction function $G(\mathbf{p})$, retaining only terms of the first order in the parameters η, L/λ. In this approximation, the operator $\hat{\Gamma}$ is absent from the equation for $G(\mathbf{p})$ and, according to (7), (8), and (13), this equation assumes the form

$$\int\frac{d^3q}{(2\pi)^3}N_q v_0\int|a(p_0,\theta_0)|^2[G_{M_2M_1}(\mathbf{p}')-G_{M_2M_1}(\mathbf{p})]\,d\Omega_0$$
$$=i[\Delta_{M_2M_1}(p)-\langle\Delta_{M_2M_1}\rangle]+i\varkappa\mathbf{v}. \tag{29}$$

We have taken the function $f_0^a(p)$ out from under the integral sign, which can be done because of energy conservation in a collision, and have cancelled it out. By (29), the angular dependence of $G_{M_2M_1}(\mathbf{p})$ can be written in the form

$$G_{M_2M_1}(\mathbf{p})=G^0_{M_2M_1}(p)+G^1_{M_2M_1}(p)\cos\vartheta, \tag{30}$$

where ϑ is the angle between $\mathbf{p}$ and $\boldsymbol{\varkappa}$. The expansion coefficients $G^0_{M_2M_1}(p)$, $G^1_{M_2M_1}(p)$ satisfy the following exact differential equations:

$$\int\frac{d^3q}{(2\pi)^3}N_q v_0\int|a(p_0,\theta_0)|^2[G^0_{M_2M_1}(p')-G^0_{M_2M_1}(p)]\,d\Omega_0=i[\Delta_{M_2M_1}(p)-\langle\Delta_{M_2M_1}\rangle], \tag{31}$$

$$\int\frac{d^3q}{(2\pi)^3}N_q v_0\int|a(p_0,\theta_0)|^2[G^1_{M_2M_1}(p')\cos\theta-G^1_{M_2M_1}(p)]\,d\Omega_0=i\varkappa v, \tag{32}$$

where θ is the angle between $\mathbf{p}$ and $\mathbf{p}'$.

The above integral equations can be solved only for extremal values of the ratios of the masses of the colliding particles: $m_a\ll m_b$ or $m_a\gg m_b$. In either case, a change in the energy of the active atom during the collision is a small fraction of the order of $m_a/m_b\ll1$ or $m_b/m_a\ll1$ of its energy prior to collision. This enables us to transform the integral equations (31) and (32) into differential equations. However, the coefficients of the differential equations and their solutions are different for the two cases. Because of lack of space, we reproduce only the final results.

The case $m_a\ll m_b$. Equation (31) becomes

$$\nu_2(p)\frac{d^2G^0_{M_2M_1}(p)}{dp^2}+\nu_1(p)\frac{dG^0_{M_2M_1}(p)}{dp}=i[\Delta_{M_2M_1}(p)-\langle\Delta_{M_2M_1}\rangle], \tag{33}$$

where

$$\nu_1(p)=\mu_a\frac{N_b\hbar}{m_a}\left(\frac{2}{3}\mu_a\langle q^2\rangle-p^2\right)\sigma_{tr}(p)+\mu_a^2\frac{N_b}{3}\langle q^2\rangle\frac{d(v\sigma_{tr}(p))}{dp}$$
$$\nu_2(p)={}^1/_3\mu_a^2N_b\langle q^2\rangle v\sigma_{tr}(p),\quad \langle q^2\rangle=2m_bT/\hbar^2, \tag{34}$$

and $\sigma_{tr}(p)$ is the transport cross section

$$\sigma_{tr}(p)=\int|a(p_0,\theta_0)|^2(1-\cos\theta_0)\,d\Omega_0. \tag{35}$$

In order of magnitude, $\nu_2(p)\sim\mu_a p^2\nu(p)$, $\nu_1(p)\sim\mu_a p\nu(p)$, where $\nu(p)=N_b v\sigma_{tr}(p)$ is the relaxation frequency of the active atom, so that both terms on the left-hand side of (33) provide the same contribution. The nonsingular solution of (33) is

$$G^0_{M_2M_1}(p)=i\int_0^p dy\int_0^y\frac{\Delta(x)-\langle\Delta\rangle}{\nu_2(x)}\exp\left[\int_x^y\frac{\nu_1(p')}{\nu_2(p')}dp'\right]dx. \tag{36}$$

Equation (32) can be transformed into an algebraic equation because the differential terms are of the order of $\mu_a\ll1$. Its solution is

$$G^1_{M_2M_1}(p)=-i\varkappa v/\nu(p). \tag{37}$$

We can now use (36) and (37) to determine the total width $\Gamma_{M_2M_1}=\langle\Gamma_{M_2M_1}\rangle+\Gamma_{M_2M_1}+\Gamma'_{M_2M_1}$. Apart from the term $\langle\Gamma_{M_1M_2}\rangle$ given by (18), we have the additional contribution

$$\Gamma^D_{M_2M_1}=\frac{2\omega^2}{3c^2}\int f_0^a(p)\frac{v^2\,d^3p}{\nu(p)(2\pi)^3}, \tag{38}$$

due to the Doppler-Dicke effect and the contribution

$$\Gamma'_{M_2M_1}=2\,\mathrm{Re}\,i\int[\Delta_{M_2M_1}(p)-\langle\Delta_{M_2M_1}\rangle]G^0_{M_2M_1}(p)f_0^a(p)\frac{d^3p}{(2\pi)^3}, \tag{39}$$

connected with the deviation of the distribution function of the atom from the Maxwell form. The broadening given

by (39) is of adiabatic origin, just as $\langle \Gamma_{M_2M_1} \rangle$.

The case $m_a \gg m_b$. Since both the change in the energy of the active atom and the angle of single scattering are small, it is convenient to start directly with (29). Expanding in powers of $(p'-p)_i$, we obtain the Fokker-Planck equation for the correction function:

$$\nu_0[m_aT\Delta G_{M_2M_1}(\mathbf{p}) - \mathbf{p}\nabla G_{M_2M_1}(\mathbf{p})] = ix v\cos\vartheta, \tag{40}$$

where the relaxation frequency is given by

$$\nu_0 = \frac{N_b}{3m_aT}\int v_0 p_0^2 \sigma_{tr}(p_0) f_0^b(p_0)\frac{d^3p_0}{(2\pi)^3}. \tag{41}$$

The angle-dependent term on the right-hand side of (40) has been omitted because it is of the order of $\mu_b \ll 1$ and gives a correction $\sim \mu_b^2$ to the width, which we have neglected.

Equation (40) has the solution

$$G_{M_2M_1}(\mathbf{p}) = -ix\mathbf{v}/\nu_0, \tag{42}$$

which enables us to determine the Doppler-Dicke width

$$\Gamma^D_{M_2M_1} = 4\omega^2 T/3c^2 m_a \nu_0. \tag{43}$$

Thus, in this case, collisional broadening reduces to the Maxwell broadening $\langle \Gamma_{M_2M_1} \rangle$. In both cases, i.e., both for $m_a \ll m_b$ and $m_a \gg m_b$, we obtain the same expressions for the shift $\langle \Delta_{M_2M_1} \rangle$ [see (16) and (17)], but different widths. When the magnetic field is not too weak, the line shape is Lorentzian, according to (24):

$$I_{M_2M_1}(\omega) = \frac{\Gamma_{M_2M_1}}{4\pi}\frac{1}{(\omega - \omega_{M_2M_1} - \langle \Delta_{M_2M_1}\rangle)^2 + {}^1/_4\Gamma^2_{M_2M_1}}. \tag{44}$$

When there is no overlap of the spectral components and (28) is valid, its difference from (44) is small and reduces mainly to a change in the total width $\Gamma_{M_2M_1}$, but the order of magnitude of this width remains the same.

The total line width $\Gamma_{M_2M_1}$ in (44) consists of a number of components. The components $\Gamma^a_{M_2M_1}$ and $\Gamma'_{M_2M_1}$ (the latter is absent for $m_a \gg m_b$) are of collisional origin. They are of the order of η as compared with the shift $\langle \Delta_{M_2M_1} \rangle$. This estimate remains valid even in the absence of Doppler broadening because it is connected only with the fact that collisional perturbations of the hyperfine-structure sublevels are small. The term $\Gamma^D_{M_2M_1}$ is due to the combined effect of thermal motion and collisions. Collisions (their number $v/L\Gamma$ is of the order of 10^4–10^7 during the emission time $1/\Gamma$) lead to a random change in the velocity of the radiating atom and thus reduce the Doppler width Γ^D by a factor of L/λ (this is the Dicke effect). As a result, we have the order of magnitude relation $\Gamma^D \sim \omega^2 v^2/c^2\nu$, where the numerical coefficient depends on the ratio of the masses of the colliding particles. The analogous Brownian narrowing down to $\Gamma^c \sim \eta^2\nu \ll |\langle \Delta \rangle|$ (as compared with the Foley estimate $\Gamma^c \sim |\langle \Delta \rangle|$) is subject to collisional broadening.

4. QUASICLASSICAL APPROXIMATION FOR THE SHIFT AND BROADENING AND SOME NUMERICAL RESULTS

The above expressions for the shift and broadening of a spectral line correspond to the exact quantum-mechanical description of binary collisions. However, under the usual conditions, the motion of the atom can be looked upon as quasiclassical, and the departure from classical motion can be taken into account in the first nonvanishing approximation as a small quantum-mechanical correction.

Let us begin by finding the classical expression for the shift. We substitute in (17) the well-known expression for the scattering amplitude in terms of the phase shifts δ_l, which, in the classical approximation, have the form

$$\delta_l^{(\mu)} = \frac{(2m)^{1/2}}{\hbar}\int_{R_\mu}^{\infty}\left\{\left[E_0 - \left(U(R) + U_\mu(R) + \frac{\hbar^2(l+{}^1/_2)^2}{2mR^2}\right)\right]^{1/2} - E^{1/2}\right\}dR - kR_\mu + \frac{\pi}{2}\left(l+\frac{1}{2}\right). \tag{45}$$

In this expression, $U(R)$ is the energy of interaction between the colliding atoms without spin correction, $U_\mu(R)$ is the addition due to the hyperfine interaction, and R_μ is the value of R corresponding to the turning point. Next, we expand the phase shifts (45) in terms of the small ratio U_μ/U, replace summation over l by integration, and take into account the fact that the hyperfine interaction is small, i.e., $|\delta_l^{(2)} - \delta_l^{(1)}| \ll 1$. Integration between l and E_0 finally yields the following result:

$$\langle \Delta_{M_2M_1}\rangle = 4\pi N_b\int_0^\infty \Delta\omega_{M_2M_1}(R)\exp\left[-\frac{U(R)}{T}\right][1+f(R)]R^2\,dR, \tag{46}$$

where $\Delta\omega_{M_2M_1}(R) = U_{M_2}(R) - U_{M_1}(R)/\hbar$

$$f(R) = \left[\frac{2}{\sqrt{\pi}}\left(\exp\frac{U(R)}{T}\right)\left(-\frac{U(R)}{T}\right)^{1/2} - \Phi\left(\left(-\frac{U(R)}{T}\right)^{1/2}\right)\right]\frac{1-\operatorname{sign}U(R)}{2}, \tag{47}$$

and $\Phi(y)$ is the probability integral. When the ratio U/T is small, we can use the simplified formula

$$f(R) = \frac{2}{3\sqrt{\pi}}\left[-\frac{U(R)}{T}\right]^{3/2}\frac{1-\operatorname{sign}U(R)}{2}. \tag{48}$$

The expression given by (46) was obtained in our previous papers[7,8] on the theory of the hyperfine line shape based on classical collisions regarded as random Poisson impacts corrected for the curvature of the trajectories of the colliding atoms. The method used in our previous papers[7,8] could not be used to obtain an unambiguous expression for $f(R)$. The formula given by (46), which is obtained from exact quantum-mechanical theory, differs from the usually employed[1-5] statistical formula by the term $f(R)$. This term is small for light pairs such as H–He (less than 1%), but for heavy pairs, it may become significant (~ 1) in the region where molecular forces change from attractive to repulsive.

To obtain the quantum-mechanical corrections to (46),

we can use an expression for the phase shifts that is more accurate than (45). A calculation, which we shall not reproduce here because of lack of space (see Batygin *et al.*[25]), has shown that the quantum-mechanical correction Δ^{qm} is equal to $0.113\langle\Delta\rangle$ in the case of H–He. The quantum-mechanical correction in the case of H–H_2 should be greater still. For active atoms heavier than hydrogen, the correction Δ^{qm} is small.

The quasiclassical expression for adiabatic broadening can be obtained from (19) in a similar way. It is

$$\langle\Gamma^a_{M_2M_1}\rangle = \frac{32N_b}{v_0}\int_0^\infty R\,dR\int_0^R R'\,dR'\,\Delta\omega_{M_2M_1}(R)\Delta\omega_{M_2M_1}(R')\,e^{-W(R')}$$

$$\times\int_c^\infty dx\,\frac{e^{-x}}{[x+W(R')]^{1/2}}\ln\left|\frac{R[x+W(R')-W(R)]^{1/2}+R'x^{1/2}}{R[x+W(R')-W(R)]^{1/2}-R'x^{1/2}}\right|, \qquad (49)$$

where $v_0=(2T/m)^{1/2}$ and we have assumed that the energy of attraction does not provide an appreciable contribution, so that $W(R)=U(R)/T$ for $U(R)>0$ and $W(R)=0$ for $U(R)<0$, $x=W(R')+mv^2/2T$. The quasiclassical expression for Γ' is obtained if we use the quasiclassical approximation for $\Delta_{M_2M_1}(p)$. Further details can be found in our previous paper.[25]

The adiabatic broadening $\Gamma^a+\Gamma'\sim\Gamma^a$ can be estimated with the aid of (46) and (49) if we note that this formula includes contributions of the regions ΔR of integration with respect to R, whose width amounts to a few Bohr radii, beginning with a value R_0 at which the exponential in our formulas reaches ~ 1 $[U((R_0)\sim T)]$. For smaller values of R, the function $\exp[-U(R)/T]$ is found to fall rapidly and, for large R, the local shift $\Delta\omega(R)$ decreases rapidly. If we use (46) to express the local shift in terms of the observed shift, $\Delta\omega(R_0)\sim\langle\Delta_{M_2M_1}\rangle/4\pi N_b R_0^2\Delta R$, we obtain the following approximate formula for the adiabatic broadening $\Gamma^a+\Gamma'$:

$$\frac{(\Gamma^a+\Gamma')\,[\mathrm{Hz}]}{p[\mathrm{Torr}]}\sim 10^{-3}\left[\frac{\langle\Delta_{M_2M_1}\rangle[\mathrm{Hz}]}{p[\mathrm{Torr}]}\right]^{2}\frac{mv_0}{R_0^2}, \qquad (50)$$

where p is the buffer gas pressure.

In conclusion, we compare some of the shift calculations based on (46) and the broadening calculations based on (49) or (50) with the experimental data (see Table I). The table is based on values of R_0 estimated as sums of the corresponding atomic radii[26] for those cases for which broadening was estimated from (50). When this was done, we adopted the experimental value of the shifts. The table lists values of $\Gamma^a+\Gamma'$ estimated from (50). The experimental value of the nonadiabatic broadening Γ^{na} is expressed in terms of the experimental value of σ^{na} for transitions to other states in the form $\sigma^{na}/N_b\bar{v}$. When there is a disagreement among the experimental data, we take the latest result (other data can be found in the review literature[18,19,21]). The collision frequency was estimated from the formula $\nu=N_b\pi R_0^2 v_0$, where $N_b=3.18\times10^{16}$ cm^{-3}. We have also estimated the values of the parameter $\eta\sim\Gamma^a/|\Delta|\sim|\Delta|/\nu$, characterizing the smallness of the hyperfine interaction and the order of magnitude of the narrowing of the line.

We note that, on the whole, the agreement between theory and experiment is satisfactory. We also note that there is a considerable difference between Γ^a and Γ^{na}, which is in conflict with the well-known Wannier model,[27] according to which $\Gamma^a\sim\Gamma^{na}$. In fact, it turns out that we have both $\Gamma^a\ll\Gamma^{na}$ and $\Gamma^a\gg\Gamma^{na}$. However, in all cases, $\Gamma^a\ll\nu$ and $\Gamma^{na}\gg\nu$ (this enables us to use the Enskog-Chapman approximation).

In the case of hydrogen, the determination of $\langle\Delta_{M_2M_1}\rangle$ from (46), using the exchange perturbation theory to find $U(R)$ and $\Delta\omega_{M_2M_1}(R)$, yields[6] $\langle\Delta_{00}\rangle=4.70$ Hz/Torr at $T=323$ °K. When the quantum-mechanical correction $\Delta_{00}^{qm}=0.62$ Hz/Torr is introduced, this result is improved as follows: $\Delta_{00}=\langle\Delta_{00}\rangle+\Delta_{00}^{qm}=5.32$ Hz/Torr, which lies within the range of experimental error: $\Delta_{exp}=5.41\pm0.25$ Hz/Torr. The theory also gives the correct temperature dependence of the shift in the broad range between 173 and 673 °K. The quantum-mechanical corrections which we have obtained improve the agreement with experiment at $T=323$ °K for the shift calculated by Davison and Liew[5] ($\Delta_{00}=5.40$ Hz/Torr), but the resultant values of Δ_{00} are too high at high temperatures ($T\sim400$–700 °K). This is explained by the fact that the variational method used by Davison and Liew[5] to determine $\Delta\omega_{00}(R)$ and $U(R)$ did not yield good enough wave functions.

The data listed in our table show, despite their incomplete character, that the theory not only provides an explanation of the experimentally established strong narrowing of the hyperfine transition lines due to Brownian motion of the active atoms during the emission process, but gives acceptable computational formulas for the line shape, shifts, and broadening. The hyperfine transition case which we have considered is thus also interesting because it enables us to complete the solution of the set of integral kinetic equations and obtain numerical results. This is in contrast to the optical case analyzed by Alekseev *et al.*,[13] which was confined to a model calculation.

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